CHEMICAL SEPARATION OF THE ISOTOPES OF URANIUM

AEC RESEARCH AND DEVELOPMENT REPORT

CHEMICAL DEVELOPMENT DEPARTMENT
CARBIDE AND CARBON CHEMICALS CORPORATION
Y-12 PLANT

OAK RIDGE, TENNESSEE
AUGUST, 1948

[redacted]

CARBIDE AND CARBON CHEMICALS CORPORATION
Y-12 PLANT CONTRACT W-7405-Eng-26

RESEARCH AND DEVELOPMENT DIVISION
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ABSTRACT

The enrichment of the isotopes of uranium has been successfully accomplished using chemical exchange reactions. Two such reactions have been utilized: the first involves a two phase liquid-liquid system in which a chloroform solution of an organic complex of uranium is contacted with an aqueous solution of tetravalent uranium ions, after the system has reached isotopic equilibrium, the phases are separated and the uranium recovered: the second is a single phase system, in water, wherein the separation of uranium is accomplished by an exchange reaction involving the exchange of uranium between U^{+4} and UO_2^{+2} ionic species.

The separation effects obtained from these two reactions (each has a factor of about 1.001) are dissappointingly low when considered from the possibility of adaptation to large scale processing, but the most significant feature of the work presented is the fact that measurable separation of the isotopes has been attained.

Extensive efforts were made to utilize the liquid-liquid system in continuous column operation. These efforts were unsuccessful primarily because of the fact that the organic complexing agent, cupferron, was subject to oxidation, and the oxidation products prevented the smooth operation of the column.

Considerable effort was made to find a more satisfactory organic compound which would be suitable for complexing the uranium and still not have the disadvantages associated with cupferron. Complete success was not attained, although the list of materials tested was large.

Future work designed to increase this separation effect is outlined.

ACKNOWLEDGMENTS

The authors wish to acknowledge the help of the following persons:

Mr. Rodger Hibbs for all determinations of mass abundance;

Dr. Douglas Hill for a number of helpful suggestions and particularly for the mathematical derivation of the rate constant.

Dr. C. C. Hurd and Mr. Parkhurst B. Wood for guidance in the statistical evaluation of the results.

Dr. C. E. Larson for his interest, suggestions, and encouragement throughout the course of the work.

INTRODUCTION

The chemical separation of isotopes has been applied successfully to a number of elements (1)* of relatively low atomic weight such as sulfur, carbon, nitrogen, and oxygen. Urey, who developed the theory and originated the method, has pointed out that chemical separation methods depend essentially upon the quantum characteristics of molecular substances (2)*. With increasing atomic weight the differences in chemical properties between isotopes or compounds of isotopes become less and less, which leads to less efficient separation by the chemical exchange process. Indeed, it has been stated by some that the method ceases to be very attractive for elements of atomic weight much above 40.

The single process separation factor which is related to the equilibrium constant in an exchange reaction usually has a value in the range of 1.01 to 1.110 and higher for the reactions involving the light elements mentioned above. With sufficient molecular spectroscopic data available these factors can be calculated with considerable accuracy as demonstrated by Urey and others (3).* By these methods the factors for reactions involving heavy isotopes can be shown to be dissappointingly close to unity.

These separation factors or equilibrium constants are calculated by the use of the values for the masses of the isotopes and the values of the vibrational frequencies of the molecules involved in the exchange. The latter are dependent in some measure upon the bonding energy between the atoms which in turn can be traced to the energy states of the outer electrons. The energy states of the outer electrons in the uranium isotopes are known to have greater differences than are ordinarily found in isotopic atoms as is evidenced by the unusually large isotopic shifts in the emission spectrum reported by Burkhart (4)*. Although highly problematical, it is conceivable that these unusually large differences might lead to a larger shift in equilibrium constant than expected in uranium isotope exchange reactions.

Even though this may not occur, it has been shown that uranium isotopes can be successfully separated by a gaseous diffusion process which utilizes a single stage factor as low as 1.004. Futhermore, as has been pointed out by Benedict, (5)* the gaseous diffusion process is considerably less efficient thermodynamically than is chemical exchange and requires application of energy at each stage of the process. In contrast a multitude of stages in the chemical exchange process can be achieved in a single packed tower or column with reflux at each end. With these advantages it seems not improbable that a chemical exchange process with a factor even lower than 1.004 might be successful.

An isotopic exchange reaction between some gas and ionic form of an element in solution apparently makes the most desireable system. Uranium presents no obvious practical system in which a gaseous compound of uranium may be exchanged with an ionic form in solution, so attention in this work was directed at liquid-liquid systems.

In the early survey work on separation methods within the Manhatten Project, some work was done on chemical methods (6)*. In those systems under study in which one phase consisted of aqueous solution, the uranium species was usually if not always the uranyl ion. Examinations of the principles and methods of calculating exchange equilibria make it evident, as noted by Bigeleisen and Mayer, (3)* that the largest factor is to be obtained by equilibrating one molecule of many bonds and high frequencies of vibration in one phase with a molecule

** Numerals in ( ) refer to references listed in bibliography.*

(or atom) of few (or no) bonds and low (or no) frequencies of vibration in the other phase. It would seem that uranyl ion which was used in these early experiments would be a poor choice for this latter species since it is known to exist (in.1N to .65N acid) with two oxygens attached with bonds believed to have covalent character (7). It would seem that the uranous ion would be a better choice for the simple species which is to be equilibrated with a complex molecule with many strong bonds and high frequencies of vibration if one disregards the waters of hydration of the uranous ion. (That this may be unjustifiable will become evident later in this discussion.)

With this in mind, a system composed of an aqueous layer containing uranous ions in contact with a chloroform layer containing uranous cupferride complex was studied. In this system a simple ion is equilibrated with a complex molecule in which the tetravalent uranium is conceivably surrounded by eight oxygens; this should give a considerable isotopic effect. The experimental results presented later demonstrate this effect but make it difficult to calculate a single process separation factor. It appears to be in the proximity of 1.001. An unsuccessful effort was made by Twichell and others to achieve a sizeable enrichment by the use of this system in column operations. This work is described in a separate report (8). In practically all the work involving cupferron, difficulties have arisen due to the instability of this compound.

A search for a more ideal complexing agent for tetravalent uranium has been underway as part of this program. A resume of this work appears herewith as Section 3. A more complete report (15) of the work on these complexing agents (without reference to isotope separation) is being prepared for more general distribution.

Molecular spectroscopic data for uranyl ion (7,9) allow a calculation to be made for the exchange of uranium between this state and the tetravalent state, if we assume the latter to be unbonded other than with weak dipole bonds in solution. Thus, using either the short method or the longer method of Bigileisen and Mayer (3) (see Appendix A), we obtain k = 1.001 for the reaction.

$$U^{238\,+4} + UO_2^{235\,+2} \rightleftharpoons U^{235\,+4} + UO_2^{238\,+2}$$

Earlier work (10) by the present authors demonstrated that under certain conditions of acidity and temperature this exchange will take place. A more complete report (11) on the study of conditions for exchange is now being issued. Other workers have since reported similar observations (12).

It seemed that a series of single stage "batch separations" based on the $UO_2^{+2} - U^{+4}$ exchange reaction would provide an interesting check on the accuracy of the calculated equilibrium constant. The experimental details of this work are presented later. The results appear to be of somewhat greater accuracy than those from the cupferron experiments but they demonstrate a shift in the equilibrium in the opposite direction to that predicted with a value for the equilibrium constant of about 1.0012. Thus if present theories are to be accepted, we must conclude that uranous ion has either more atoms bonded to it than UO_2^{+2} or that those bonds which it does possess are much stronger than those in the uranyl ion. Either conclusion is somewhat difficult to accept. A spectroscopic investigation of aqueous tetravalent uranium is now underway in an attempt to observe Raman shifts. The extreme absorption of U^{+4} ion makes this somewhat difficult.

It is evident, of course, that the uranous-uranyl exchange reaction with both ions present in the aqueous phase could not be used in any continuous column operating process for separating isotopes. However, the fact that the U^{235} shift is to the UO_2^{+2} form seems to provide an attractive possibility. Consider the following equilibria:

$$U(Complex)_4 \rightleftharpoons U^{+4} \rightleftharpoons UO_2^{+2}$$

The U^{235} tends to go to the right in both equilibria and with a system involving all three species we should achieve an exchange between $U(Complex)_4$ and UO_2^{+2} in two phases with an equilibrium constant which is the product of the two separate equilibrium constants. This should be approximately 1.0022 in magnitude. The maximum value for this double exchange would be approached most closely in actual use when the ratio of UO_2^{+2} to U^{+4} is greatest in the aqueous phase. Unfortunately this is also the condition which makes the rather slow $U^{+4} - UO_2^{+2}$ exchange even slower. Studies are under way now to find a means of catalyzing this exchange reaction.

Evaluation of this work at this time seems difficult. However, the laboratory work and the column studies by Twichell (Section 2) have provided some small basis for making some very preliminary calculations on cost of construction and operation of a chemical exchange plant. Such calculations have been made by John Shacter and others in the K-25 theoretical analysis department under Dr. George Garrett which indicate that a single stage separation factor as low as 1.001 would lead to prohibitive cost. Other important factors leading to high cost were the low concentrations of uranium in the solutions used, and the length of a theoretical stage (three feet) estimated from the column studies. With increased concentrations and other improvements it seems possible that a factor approaching 1.003 might lead to an economical process if the complexing agent and all solvents could be recycled efficiently.

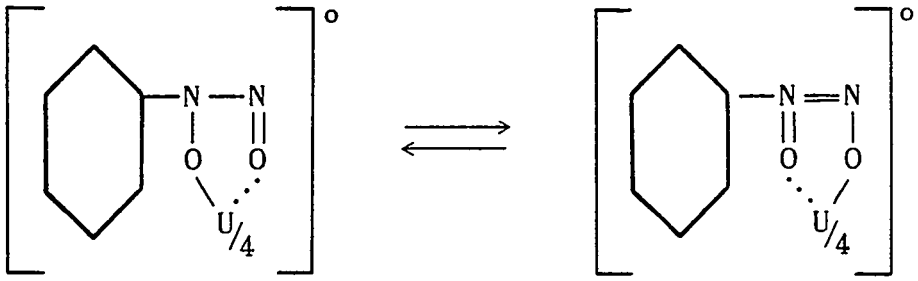
Further laboratory work will be aimed at establishing definitely whether or not there is any real possibility of achieving a factor as high as 1.003.

SECTION 1

EXPERIMENTAL

Separation of Uranium Isotopes by the $U^{+4} \rightleftharpoons$ Uranous Cupferride Exchange.

The greater part of the experimental work carried out to date makes use of the cupferron complex of uranium. It is a typical inner complex and may be pictured as an equilibrium between two tautomeric forms.



As is true in other cases of inner complex organo-metallic compounds, uranous cupferride is insoluble in water but soluble in non-polar organic solvents. This makes possible a two phase system in which uranium may exchange between its cupferron complex in an organic solvent such as chloroform and the ionic form (U^{+4}) in aqueous solution.

The first point checked was to determine if the uranium does exchange between its ion and cupferron complex. By means of tracer technique, it was found that exchange does take place. The details of this experiment are treated in Appendix B. Suffice to say at this point, the rate of exchange was fast enough for our purpose.

The first batchwise run (13) was carried out by dissolving about 800 grams of UCl_4 in 1N HCl to give a 3% uranium solution. Sufficient cupferron was then added (2.5 Moles. Cup./Mole U) to cause a 50% extraction of the U^{+4} into a volume of chloroform equal to that of the aqueous solution. The two phase system was thoroughly agitated for fifteen minutes. This allowed time for the isotopic reaction to reach equilibrium.

$$U^{238\ +4} + U^{235}(C_6H_5N_2O_2)_4 \rightleftharpoons U^{235\ +4} + U^{238}(C_6H_5N_2O_2)_4$$

According to theory the lighter isotope favors the ionic, U^{+4}, state and should concentrate in the aqueous phase. The separation produced would be equal to one simple process factor often designated by α.

$$\alpha = \frac{\frac{U^{235}}{U^{238}} \text{ in aqueous phase}}{\frac{U^{235}}{U^{238}} \text{ in organic phase}}$$

$$\alpha = (\text{approx.}) \frac{\%\ U^{235} \text{ in the uranium of the aqueous phase}}{\%\ U^{235} \text{ in the uranium of the organic phase}}$$

Since assay methods were not reliable enough to detect the single separation factor more than one stage was carried out.

This was done by recovering the uranium from the aqueous phase, reducing to the U^{+4} state over zinc in dilute HCl and repeating the cycle previously des-

cribed. After carrying out eight such stages the final sample was submitted for assay. Results on the starting material and product indicated an increase from .7060% U^{235}, the starting material, to .7093%, the product. This enrichment in eight stages corresponds to a simple process factor of 1.0011. This series was reported in detail in Y-41 (13).

This factor was encouraging in view of the fact that experimental difficulties were encountered in the process. The most serious difficulty was that of the decomposition of cupferron causing objectionable tarry products, oxidation of some U^{+4} to UO_2^{+2}, etc. Another disadvantage was the presence of zinc in the aqueous phase. It was necessary to perform a chemical separation to get rid of the zinc in the final stages.

It was felt that if another run was carried out, minimizing or eliminating the above difficulties, a still better separation factor might be obtained. To minimize decomposition the change was made in the procedure of cooling the system down to 5^{o}-10^{o}C. Instead of using zinc to reduce the uranium it was prepared as UCl_4 after each stage by the hexachloropropene reaction (14). A flow diagram for one stage is shown in Fig. 1, and results shown in Table 1.

The increase in U^{235} concentration from .705% to .708% gives a separation factor of 1.0010 per stage. This is in fair agreement with that of the previous run; it did not show as high an alpha factor as had been hoped.

Although the results of the runs are in reasonable agreement and would seemingly establish $\alpha = 1.001$, an objection may be made in the case of either run: this is the possibility of contamination. Both enrichment runs were carried out in laboratories in which small amounts of uranium well above normal in U^{235} concentration had been handled in the course of various special experiments. Even though all reasonable precautions were taken to avoid contaminating the samples, the chance that this could happen is admittedly real, though rather remote.

Two ways were suggested in which a run might be carried out in order to minimize the objection to contamination. First, a run could be carried out using uramium containing about 10% U^{235} which would thus mitigate the effect of any chance contamination. Second, a run following the uranium in the organic phase could be recycled; this would produce slightly depleted material if a separation effect exists.

The second approach was decided as being the more satisfactory although it is still subject to the objection that chance contamination could nullify or effectively reduce the depletion effect.

Two "depletion" runs were carried out, and the results appear in Tables 2 and 3 respectively.

The separation factors computed from the depletion runs are both less than those obtained from the enrichment runs. This cannot be accounted for readily unless one assumes chance contamination nullifying the separation effect.

Possibly the most significant conclusion which may be derived from the forgoing runs is that there is evidence of a separation of the isotopes-admittedly quite small however.

Because of the instability of cupferron its use has been abandoned in these runs. Other organic complexing agents are being investigated. A brief discussion of this work is found in Section 3. If any suitable complexing agent is found, batch runs similar to the cupferron runs will be made to determine the amount of isotope separation.

FIGURE 1

Flow Diagram of One Stage

of the U^{+4} - $U(C_6H_5N_2O_2)$ Process

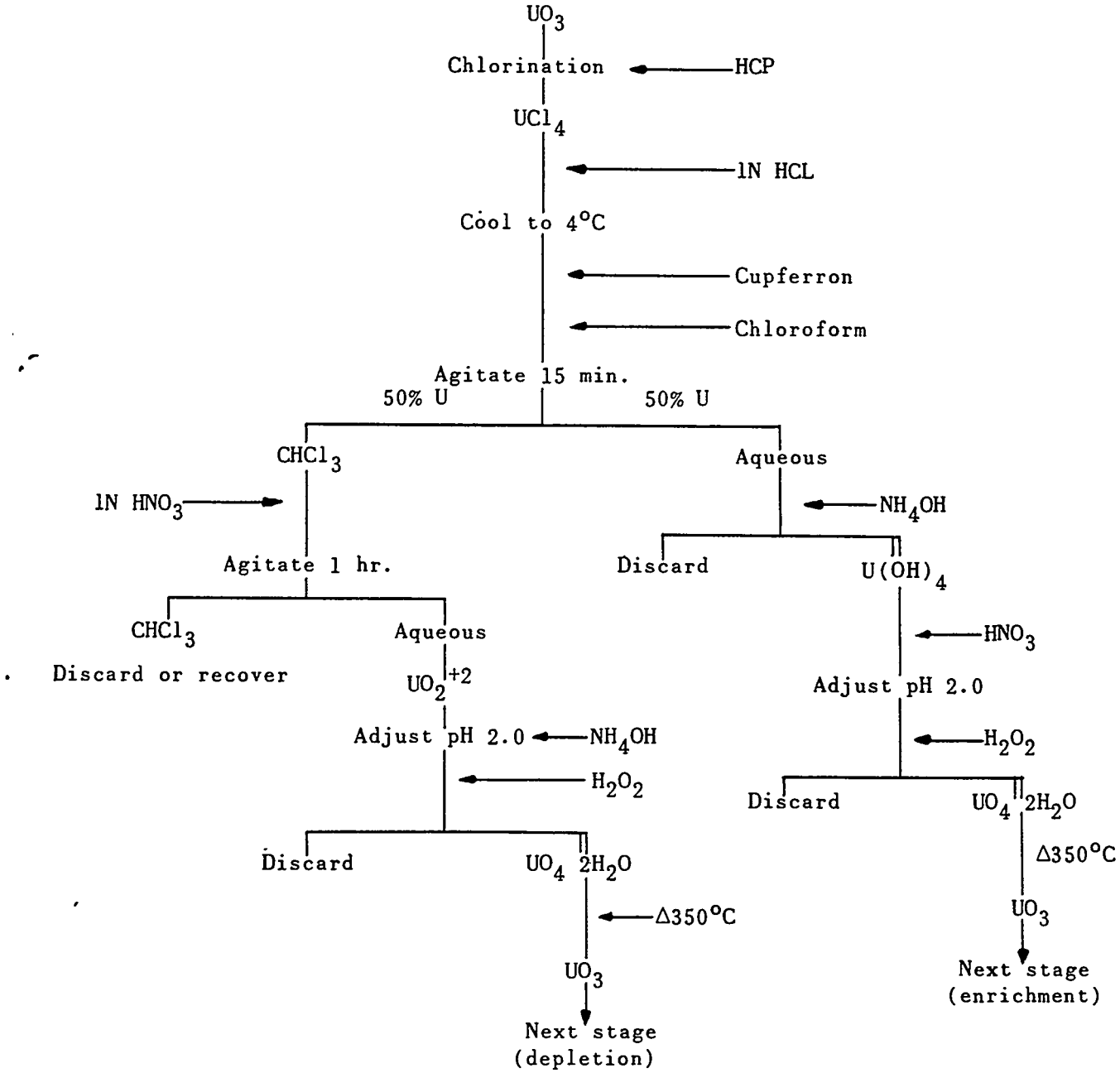


Table 1 sums up the run using the lower temperature and hexachloropropene reduction.

TABLE 1

Enrichment Run Based on $U^{+4} \rightleftarrows U(C_6H_5N_2O_2)_4$ Exchange

(Low temperature, H. C. P. Reduction)

Stage	Total Vol. ml.		HCL in Aqueous ml.	Uranium in Aqueous g	Cupferron Added to Aqueous g	Temperature of Extraction	Assay of Sample Ave. % U^{235}
	AQ	$CHCL_3$					
Start	-	-	-	-	-	-	.7052
1	26,700	26,700	2,200	800	1,300	10°C	-
2	26,700	26,700	2,200	400	488	10°C	.7052
3	10,000	10,000	833	200	244	6°C	.7070
4	2,900	2,900	241	85	114	4°C	.7077
5	1,367	1,367	114	42	47	9°C	.7082
6	673	673	56	21.2	23	9°C	.7083
7	337	337	28	10	11.6	9°C	-
8	169	169	14	5	5.8	9°C	.7064
9	85	85	7	2.5	3.0	9°C	.7081

TABLE 2

Depletion Run (#3) using $U^{+4} \rightleftarrows U(C_6H_5N_2O_2)_4$

(HCP Reduction-Low Temperature)

Stage	Total Vols ML		HCl(conc) in Aqueous	Uranium in Aqueous Before Ext.	Cupferron Added to Aqueous	Temp. of System	Assay of Sample % U^{235} Ave.
	Aq.	$CHCl_3$					
Start	-	-	-	-	-	5°-10°C	-
1	26,700	26,700	2,200	400	-	5°-10°C	.7067
2	6,600	6,600	550	198	258	5°-10°C	-
3	1,600	1,600	133	47.8	94	5°-10°C	.7061
4	1,083	1,083	90	32.5	60	5°-10°C	.7070
5	593	593	49	17.8	33	5°-10°C	-
6	393	393	33	11.3	20	5°-10°C	-
7	201	201	17	6.0	10	5°-10°C	-
8	103	103	9	3.1	5	5°-10°C	.7042 .7042

TABLE 3

Depletion Run (#4) using U^{+4} - $U(C_6H_4N_2O_2)_4$ Exchange

(H.C.P. Reduction - Room Temperature)

Stage	Total Vols. ml.		HCl (conc) in Aqueous m.l	Uranium in Aqueous Before Ext.	Cupferron Added to Aqueous	Temperature of Extraction	Assay of Sample % U^{235} Ave.
	Aq	$CHCl_3$					
Start	-	-	-	-	-	-	-7052
1	26,700	26,700	2,200	800	1,300	28°C	.7052
2	10,900	10,900	833	328	535	28°C	.7054
3	6,100	6,100	508	183	298	28°C	.7055
4	3,200	3,200	266	96.5	156.7	28°C	
5	1,580	1,580	132	47.4	77.6	28°C	.7030
6	786	786	66	23.6	38.8	28°C	
7	397	397	33.1	11.9	19.4	28°C	
8	203	203	17.0	6.1	9.7	28°C	
9	103	103	8.6	3.1	5.0	28°C	.7045 .7044

Separation of Uranium Isotopes by The U^{+4} - UO_2^{+2} Exchange Reaction.

An investigation carried out by this group on the exchange of Uranium between U^{+4} and UO_2^{+2} ions in dilute hydrochloric acid has been published in other reports. The question arose whether a series of batch separations would give a value for the equilibrium constant in agreement with the calculated value. A simple form of the exchange is given by the equation:

$$U^{235\ +4} + UO^{238\ +2} \rightleftharpoons U^{238\ +4} + UO_2^{235\ +2}$$

The rate of interchange of uranium isotopes depends on conditions of hydrogen ion concentration and temperature. It is sufficient to note here that at room temperature the exchange will take place within a pH range of 1.0 to 2.0. Further discussion of this is found in Appendix C.

The following procedure was used for a stage in this process: A quantity of uranium oxide (UO_3) of known isotopic concentration (normal at the start of a run) was divided into two equal portions. One of these was chlorinated to UCl_4 with hexachloropropene, the other was prepared as $UO_2Cl_2.XH_2O$ by dissolving UO_3 in hydrochloric acid and evaporating to dryness on the hotplate.

The two salts, UCl_4 & UO_2Cl_2, were then dissolved in a sufficient quantity of water to give a 4% uranium solution, i.e. 2% with respect to U^{+4} and 2% U as UO_2^{+2}. The pH of the solution was checked at this point and usually it was 1.5 which is in the acid range where exchange takes place.

Sufficient time, one to two hours, was allowed for the system to come to equilibrium. The exchange reaction was stopped at this point by the addition of a sufficient quantity of hydrochloric acid to raise the normality to 3N. A five percent excess over the theoretical amount of oxalic acid necessary to precipitate all U^{+4} ion was added and the solution stirred to aid in the formation of an easily filtered uranous oxalate precipitate. The oxalate precipitate was washed several times with dilute HCl containing oxalic acid, combining these washings with the original filtrate. After this step the uranium was recovered from either phase and processed to UO_3 at which point it is ready for the succeeding stage.

The flow sheet of these operations has been presented in Figure 2.

In the case of a depletion run the uranium from the oxalate precipitate is recycled while an enrichment run is carried out by following the aqueous phase, or uranyl ion.

The possibility that exchange of uranium could conceiveably take place between UO_2^{+2} ion and $U(C_2O_4)_2$ was checked. No exchange was found under the conditions described in the stage procedure. The details of this experiment are found in Appendix D.

An enrichment run was carried out using the above procedure; results are found in Table 4 and Fig. 3. Results of a depletion run are presented in Table 5 and Figure 3.

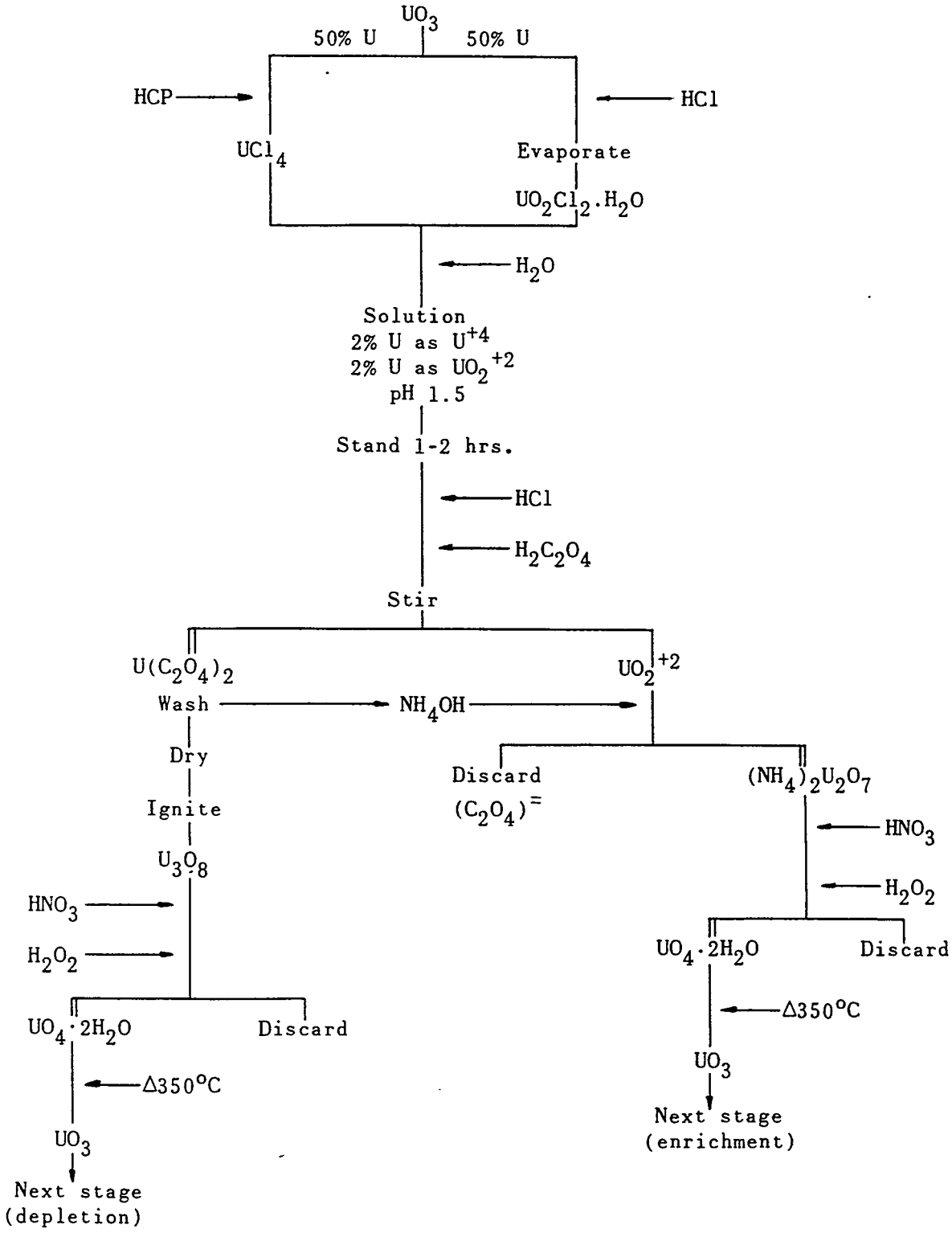
A statistical treatment of the entire data is given in Appendix E.

A separation factor of about 1.0012 may be computed from either the enrichment or depletion run. The good agreement makes this system quite attractive as a basis for future work.

FIGURE 2

Flow Diagram of One Stage of

The U^{+4} - UO_2^{+2} Exchange Process



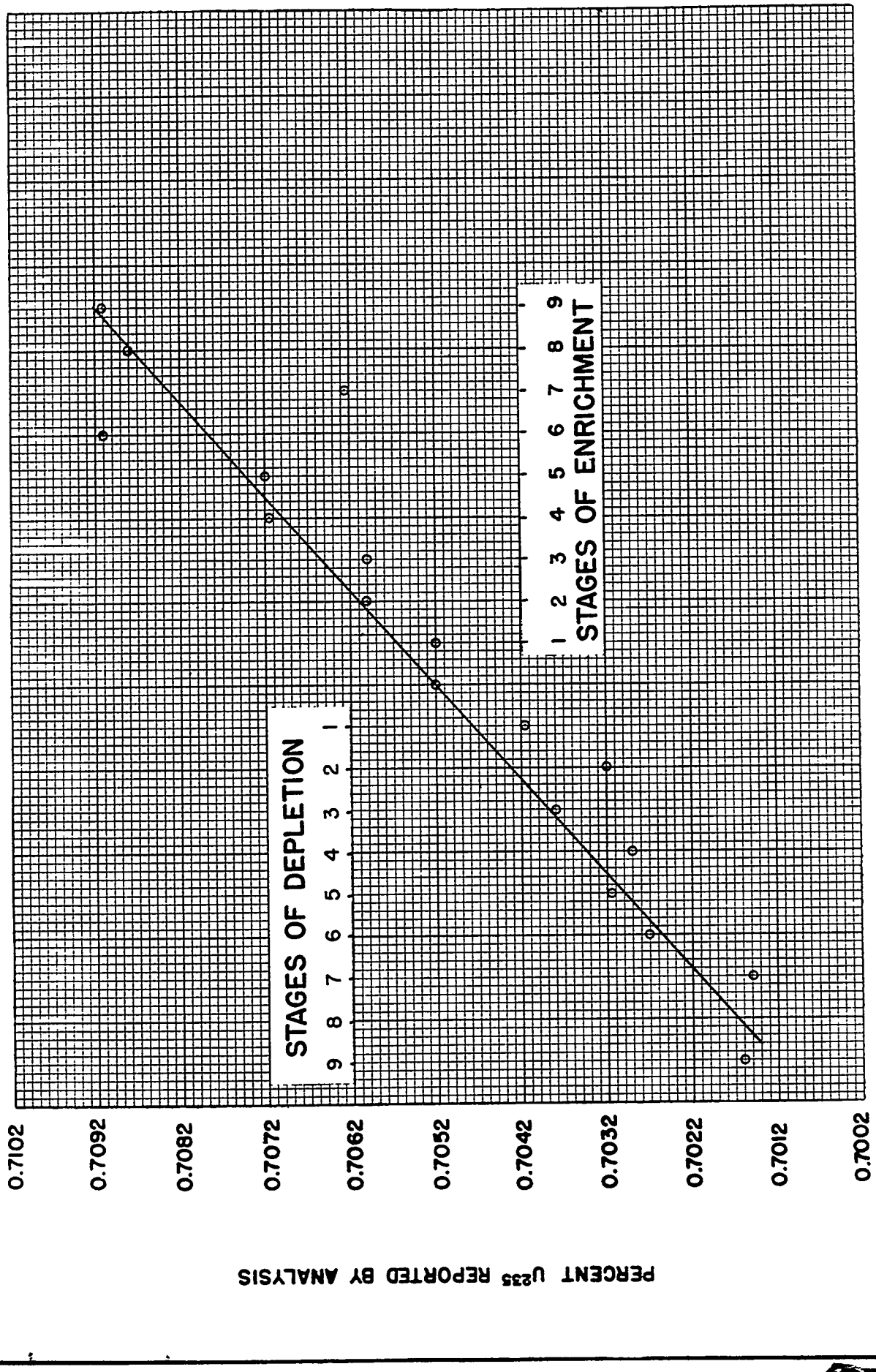


FIGURE 3- ENRICHMENT OR DEPLETION
STAGE USING U^{+4} - UO_2^{+2} EXCHANGE SYSTEM
VS

TABLE 4

Enrichment Run Using U^{+4} - UO_2^{+2} Exchange (Following UO_2^{+2})

Stage	Total U in grams		Total Volume of System (Ml)	pH	Time of Stand (Min.)	Temp. °C	Ml Conc. HCl Add. at end of Exchange	Oxalic Acid Add. to PPT U^{+4} (g)	Assay of Samples % U^{235}
	As U^{+4}	As UO_2^{+2}							
0	-	-	-	-	-	-	-	-	.7052
1	396	399	40,000	1.55	60	28-30	5,000	480	.7052
2	198	198	20,000	1.68	60	28-30	2,500	239	.7058
3	96	96	9,600	1.53	60	28-30	1,500	115	.7058
4	47	46	4,600	1.55	60	28-30	750	57	.7071
5	23	22.5	2,200	1.55	60	28-30	375	28	.7072
6	10.8	10.8	1,080	1.56	60	28-30	180	13.1	.7090
7	5.5	5.2	700	1.40	120	28-30	125	6.7	.7063
8	3.5	3.5	350	1.49	90	28-30	60	4.2	.7086
9	1.6	1.6	160	1.52	60	28-30	26	2.0	.7090

TABLE 5

Depletion Run Using U^{+4} - UO_2^{+2} Exchange (Following U^{+4})

Stage	Total U in grams		Total Vol. of System Ml	pH	Time of Stand (Min)	Temp. °C	Ml Conc. HCl Added	g Oxalic Acid Added	Assay (ave) % U^{235}
	As U^{+4}	As UO_2^{+2}							
0	-	-	-	-	-	-	-	-	.7054
1	399	399	20,000	1.60	75	28-30	5,000	481	.7041
2	164	145	7,750	1.55	60	28-30	1,940	198	.7032
3	82	54	4,000	1.53	60	28-30	1,350	100	.7038
4	47	32	1,975	1.55	70	28-30	650	60	.7029
5	22.4	18.4	1,018	1.51	60	28-30	350	30	.7031
6	12.8	10.9	593	1.55	65	28-30	200	16	.7027
7	5.6	4.8	308	1.57	70	28-30	100	8	.7015
8	2.7	2.4	153	1.58	65	28-30	50	4	-
9	1.6	1.5	78	1,51	75	28-30	25	2	.7016

Accuracy of Method of Assay

Because of insufficient spectroscopic data no theoretical estimate of the equilibrium constants and enrichment factors could be made for the systems used. This places the significance of the results on the accuracy of the method of assay.

All uranium assays were carried out on the samples (UF_6) in a modified Nier spectrometer. In order to obtain some indication of the accuracy of the assay, control samples were submitted along with the experimental samples. The control samples ranged in uranium concentration from .700% U^{235} to .710% U^{235} increasing in .001% increments.

The preparation of the "enriched" control samples was carried out by combining known amounts of enriched uranium (13.2% U^{235}) and normal (.7052% U^{235}) material in solution form. The uranium was then precipitated from the solution and ignited to U_3O_8. "Depleted" standards were prepared in an analogous manner except that below normal (.05% U^{235}) was used to dilute normal (.7052% U^{235}) material.

The assay results of these standards are given in Table 6 and Figure 4,

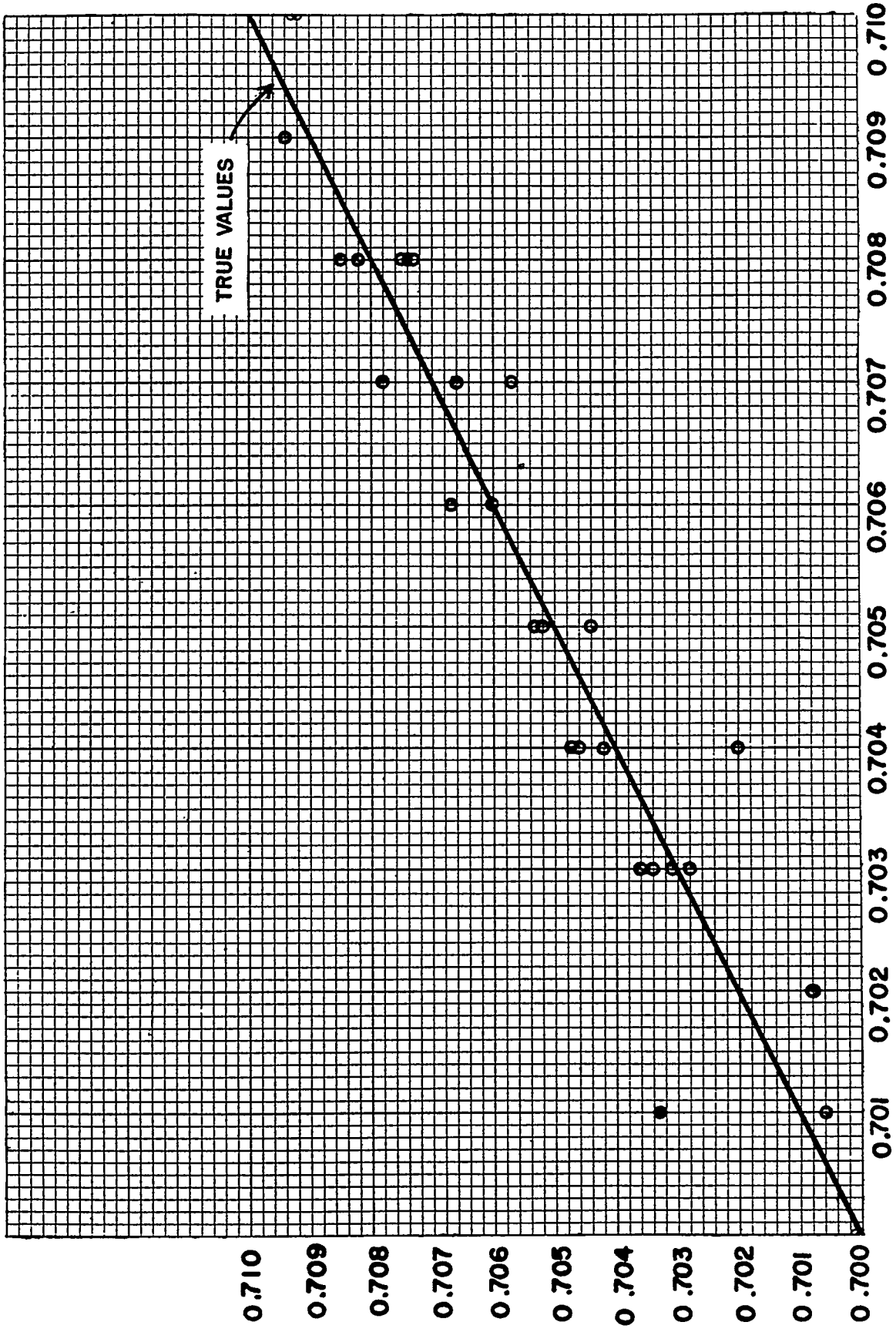


FIGURE 4 ASSAY RESULTS vs STANDARD

TABLE 6

RESULTS OF ASSAYS

STANDARD % U^{235}	AVERAGE RESULT OF ASSAYS %U^{235}
.700	.7004
.701	.7006; .7033
.702	.7027; .7030; .7031
.703	.7052; .7033; .7034; .7028; .7036
.704	.7027; .7047; .7020; .7042
.705	.7051; .7053; .7052; .7053; .7044
.706	.7083; .7061; .7067; .7060
.707	.7057; .7070; .7066; .7078
.708	.7075; .7073; .7082; .7074; .7085
.709	.7095; .7094
.710	.7092; .7087

SECTION 2

CHEMICAL EXCHANGE COLUMN OPERATION USING THE SYSTEM

$$U^{238\ +4} + U^{235}(\text{cupferride})_4 \rightleftharpoons U^{235\ +4} + U^{238}(\text{cupferride})_4$$

INTRODUCTION

Laboratory and theoretical work leading up to column operation was previously reported in project report Y-41. Batch experiments were carried out, and a single stage separation factor of 1.0014 was reported. Since that time other batch experiments have indicated that the value is more nearly 1.0010 or slightly less. The factor being of a small magnitude made it impossible to attain any sizeable enrichment by batch separation. Therefore, it was decided to attempt column operation in order to attain a larger number of stages and show a greater enrichment. Thus, the limitations on accuracy of the mass spectrograph assay would not appreciably affect the measurement of total enrichment as was the case in batch separations.

Theory and experimental work showed that the U^{235} tended to build up in the aqueous phase. Therefore it was proposed to feed the U^{+4} ion in aqueous solution to the bottom of a packed column, convert it to $U(\text{cupferride})_4$ in $CHCl_3$ solution at the top of the column, and send this organic solution down in countercurrent contact with the rising aqueous phase. The column was to be operated in this manner long enough to bring it to equilibrium at which time samples for assay were to be taken from the top (enriched end) of the system. Equilibrium time calculations were made using general formulas derived by H.C. Urey for chemical exchange systems. An example of such a calculation for this system is given in report Y-41.

EXPERIMENTAL METHODS

Original Apparatus

The apparatus for the first series of runs consisted of a glass column thirty feet in length and one centimeter inside diameter. It was packed with 3/16-inch pyrex helices and covered with 3-inch cork insulation. Auxiliary equipment included a 15-gallon, glass lined feed tank, small glass receiving and head tanks, rotameters, and a water cooler.

Procedure Used for First Runs

The aqueous UCl_4 solution (1.5% U, 1.5 N HCl) was discharged from the feed tank by N_2 pressure, metered at 10 c.c. per minute, pre-cooled to 10°C., and fed into the bottom of the column as the continuous phase. Upon reaching the top of the column, the aqueous solution was collected in a cooled receiver tank, periodically drawn off, and hand extracted with $CHCl_3$ and an excess cupferron. The $CHCl_3$ layer was then placed in a cooled head tank and metered into the top of the column at 10 c.c. per minute. This organic solution was continuously drawn off the bottom of the column and stored. All solutions were kept cold and under a nitrogen atmosphere to avoid decomposition of U(cupferride)$_4$ and oxidiation of U^{+4}.

Two runs of this type were made, and both had to be terminated because of decomposition in the organic phase. The longest run was of 24-hours duration. During this time operation was not satisfactory in that periods of flooding and channeling took place. Assay results showed a feed concentration of 0.7062% U^{235} and a product concentration of 0.7074%. This was not considered a significant increase. The difficulties encountered indicated that considerable development work was yet necessary before more column runs could be made.

Laboratory Studies to Develop Improved Conditions of Column Operation

Automatic Reflux. Considerable work was done to develop a device to automatically convert U^{+4} aqueous solution to U(cupferride)$_4$ in $CHCl_3$ solution at the top of the column. The following types of mechanism were tested: (1) Small spinner type extractor with a water solution of cupferron entering concurrently with the aqueous UCl_4 and $CHCl_3$ passing through countercurrently. Result: Incomplete removal of U^{+4} from aqueous phase. (2) Liquid-liquid centrifuge with solutions entering in the same manner as above. Result: Incomplete extraction. (3) Mixing of the three solutions in a throttled centrifugal pump discharging into a settling tube for separation of phases. Result: Decomposition and incomplete extraction. (4) Dripping UCl_4 solution and $CHCl_3$ through a deep bed of of solid cupferron followed by a settling tube. Result: Decomposition and plugging of filter supporting the cupferron. (5) Mixing the three solutions by mechanical stirring in two mixing tubes followed by a settling tube. Result: Complete extraction of U^{+4}. The last type of system proved to be the only one showing promise. The device and modifications of it were used for subsequent column runs. A drawing of the mechanism in its final modified form is shown in in Figure 5.

Test Runs in Small Laboratory Column. A four-foot by one-centimeter column was used to study types of flow required to eliminate flooding and channeling and to get most efficient contact between phases. The four possible types of flow were tested to see which would afford most satisfactory operation. The

results are shown in Table 7.

Table 7

Flow Type	Result
Aqueous continuous and wetting. $CHCl_3$ discontinuous.	$CHCl_3$ channeled in droplets. No flooding.
Aqueous continuous. $CHCl_3$ discontinuous and wetting.	$CHCl_3$ channeled in droplets. Flooding.
$CHCl_3$ continuous and wetting. Aqueous discontinuous.	Aqueous channeled in droplets. Flooding.
$CHCl_3$ continuous. Aqueous discontinuous and wetting.	Aqueous flowed in layers over packing. No flooding or channeling.

All flow rates were held as nearly as possible at 10 cc per minute in both phases. The last set of conditions appeared to afford the most satisfactory operation.

- It was decided to obtain a comparison between the amount of surface contact afforded by layer and droplet flow. This was achieved by measuring the amount of extraction at equilibrium in the four-foot column using the two types of flow. The system used was that of $UO_2(NO_3)_2$ aqueous solution and dibutyl carbitol. The aqueous phase was salted with enough $Al(NO_3)_3.6H_2O$ to give an extraction coefficient of 2.95. All conditions were held constant except the flow type in the discontinuous phase. Samples of aqueous phase were periodically analyzed for uranium until the concentration became constant, indicating equilibrium. The results of the comparison are shown in Table 8.

Table 8

Flow Type	$\frac{U \text{ in Organic}}{U \text{ in Aqueous}}$
Aqueous discontinuous, wetting and flowing in layers.	3.56
Aqueous wetting. Organic discontinuous and flowing in droplets.	0.77

It was logical to assume that since layer flow gave more extraction in a given column length, it would also result in more exchange. All subsequent column runs were made using conditions giving layer flow in the aqueous phase. A number of short runs were made on the four-foot column using the automatic refluxer previously described. Decomposition in the organic phase continued to be a major source of trouble. It was discovered during these test runs that the cause of decomposition was due to the excess cupferron forming the very unstable, $CHCl_3$ soluble, acid cupferride. The presence of this compound (nitroso phenyl hydroxylamine) in the $CHCl_3$ phase offered two difficulties: (1) decomposition accompanied by violent gassing, and (2) ability of acid cupferride to extract uranium from the aqueous phase in the column.

Attempts to Remove Excess Cupferron. A number of tests were made using various solutions in an attempt to wash the excess cupferron from the organic phase. The efficiency of removal was measured by shaking the organic phase, after washing, with a standard UCl_4 solution. Any decrease in uranium concentration in the standard solution was caused by incomplete removal of the excess cupferron. The results of this work are shown in the following table.

Table 9

Wash Solution	Results
H_2O	No removal of cupferron.
Dilute NH_4OH	Emulsion and precipitate formed.
$NH_4C_2H_3O_2$	No removal of cupferron.
Fe^{+3}	97% removal. Some U lost to aqueous wash.
Cd^{+2}	Incomplete removal.
Al^{+3}	92% removal. Some U lost to aqueous wash.
Sn^{+4}	88% removal. Some U lost to aqueous wash.
Cu^{+2}	Cu(cupferride)$_2$ did not meet solubility requirements.

In each case there was used more than enough wash reagent to remove all of the excess cupferron if the reactions had been quantitative. Fe^{+3}, and Sn^{+4} removed most of the excess cupferron, but its removal apparently rendered the formation of U(cupferride)$_4$ incomplete allowing some U^{+4} to pass into the aqueous wash solution. This factor ruled out the chance of removing excess cupferron by means of an aqueous wash. The only alternative appeared to be the minimizing of excess cupferron in the $CHCl_3$ phase. This was accomplished by adding less than the theoretical amount of cupferron in the automatic refluxer. The aqueous effluent was then analyzed for uranium and a slight excess of cupferron was added along with $CHCl_3$. A hand extraction was then made, and the organic layers from both refluxes and hand extraction were combined and returned to the top of the column. In this way only a small amount of excess cupferron passed into the organic phase.

Modified Thirty-Foot Columns

A new thirty-foot by one-centimeter column was constructed. It was built in six sections, each equipped with a blown glass water jacket. All solutions were fed to the system by means of Sigmamotor constant delivery rate pumps. These pumps operated on the principle of squeezing the solution through a heavy wall, gum rubber tube. Operation was very satisfactory even when working against a thirty-foot head of $CHCl_3$ (20 psi). Several runs were made using the reflux procedure outlined in the previous paragraph. In all runs an appreciable amount of uranium remained in the effluent even after the second extraction. This was thought to be due to oxidation of the effluent from the first extraction. It was necessary for the solution to stand for approximately thirty minutes before the analysis and hand extraction could be made. Some flooding occurred which was probably due to constrictions in the one-centimeter tube or gaps in the packing.

In order to obtain a more uniform bore column and even stacking of helices, another column was constructed of one-inch pyrex pipe, water jacketted with two-inch pyrex pipe. No flooding occurred during the operation of this column. It

also afforded a more sturdy structure, and there was no glass breakage as had previously been encountered. A different reflux procedure was used which involved a two-stage automatic device (Figure 5). The excess cupferron was held to a minimum. A variable speed transmission was connected to the cupferron solution pump so that the rate of delivery to the refluxer could be adjusted when necessary. Thus when the UCl_4 solution at the top of the column began to fade in color, (indication of excess cupferron extracting U in the column) the pumping speed was reduced until the normal color returned to the solution. Constant flow rates of 16 and 22 cc per minute were used for the UCl_4 solution and $CHCl_3$ respectively. A flow diagram of the apparatus is shown in Figure 6.

The results of the runs made using the new procedure showed that losses still occurred in the extracted effluent from the refluxer. During 16 hours of operation (calculated equilibrium time) a total of 239 grams of uranium was fed to the system. Seventeen grams, or seven percent, of the total were lost to the effluent. Samples of UCl_4 solution were taken at the bottom of the column and at the top and analyzed for UO_2^{+2} concentration. An averare of approximately one mg uranium per ml solution was oxidized in passing through the thirty-foot column.

Attempt to Hold U^{+4} in Reduced State

Studies were made of the effect of increased acid concentration on the oxidation of UCl_4 solution in contact with U(cupferride)$_4$ in $CHCl_3$. The effect of degassed solvents on oxidation was also measured. One-hundred ml portions of UCl_4 solution (1.5% U) were shaken for five minutes with 100 ml of U(cupferride)4 in $CHCl_3$. The aqueous layer was analyzed for UO_2^{+2} before and after shaking. The following table shows the effect of acid concentration and degassed solvents on oxidation.

Table 10

Conditions	Increase in UO_2^{+2} (mg U/ml)
(Blank) 1.5 N HCl	2.45
2.0 N HCl	1.31
2.5 N HCl	0.39
3.0 N HCl	0.70
3.5 N HCl	0.62
1.5 N HCl, degassed $CHCl_3$	1.68
1.5 N HCl_3 degassed water and $CHCl_3$	1.13

Except for one erratic result at 2.5 normal acid, there was a trend toward slower oxidation at higher acid strength. Degassed solvent also slowed the rate of oxidation, but neither device was sufficient to completely eliminate it.

The addition of a reducing agent, sodium formaldahyde sulfoxalate ($NaSO_2 \cdot CH_2OH.2H_2O$), to the aqueous phase showed good possibilities in laboratory tests. The reagent was found to be capable of reducing UO_2^{+2} quite rapidly. Therefore, the reducing agent should be preferentially oxidized in the column leaving the U^{+4} in its reduced state. The one disadvantage exhibited by this compound was that it reduced the efficiency of the $CHCl_3$-cupferron extraction in the refluxer. The reason for this was not determined.

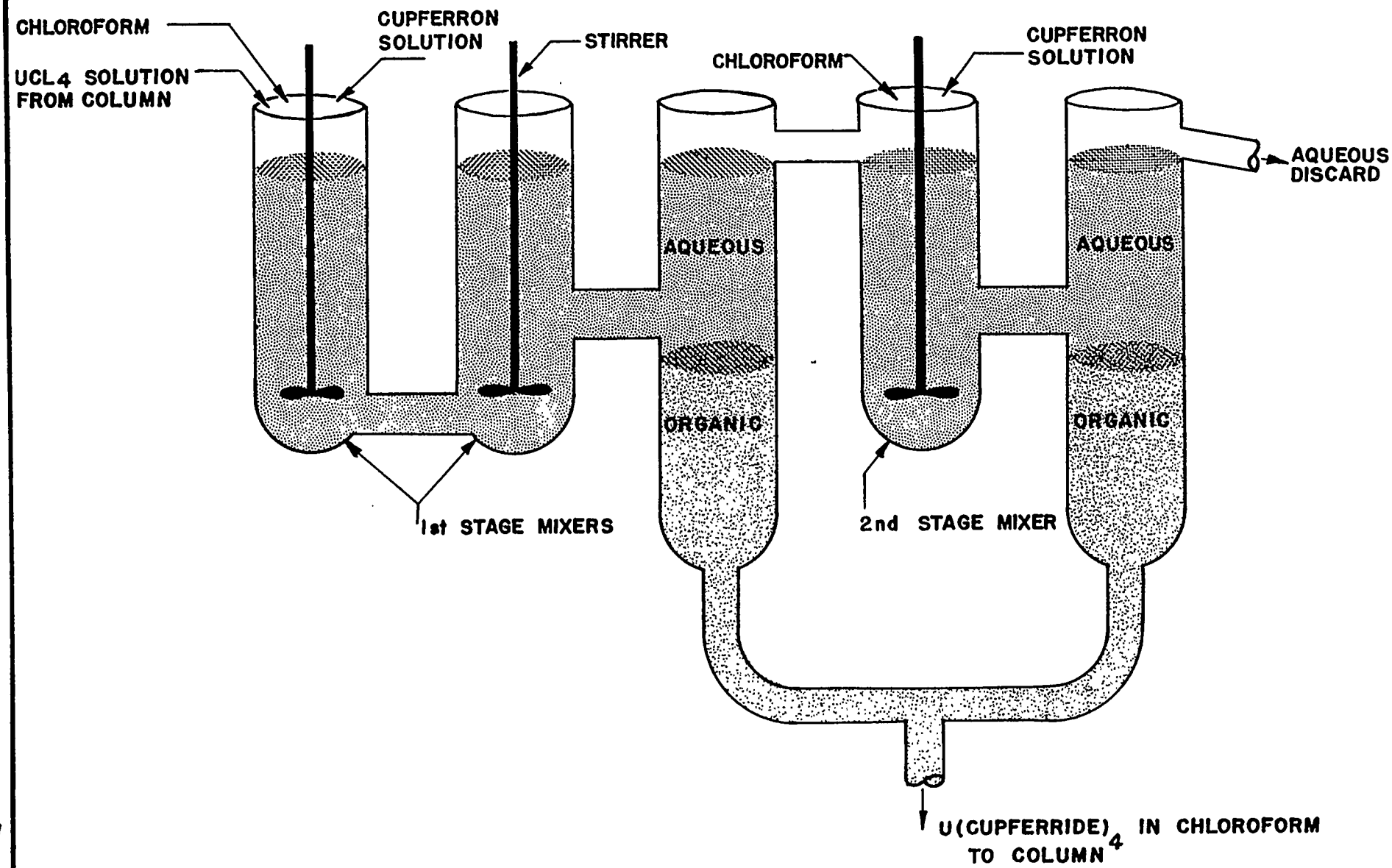


FIGURE 5- AUTOMATIC REFLUX DEVICE

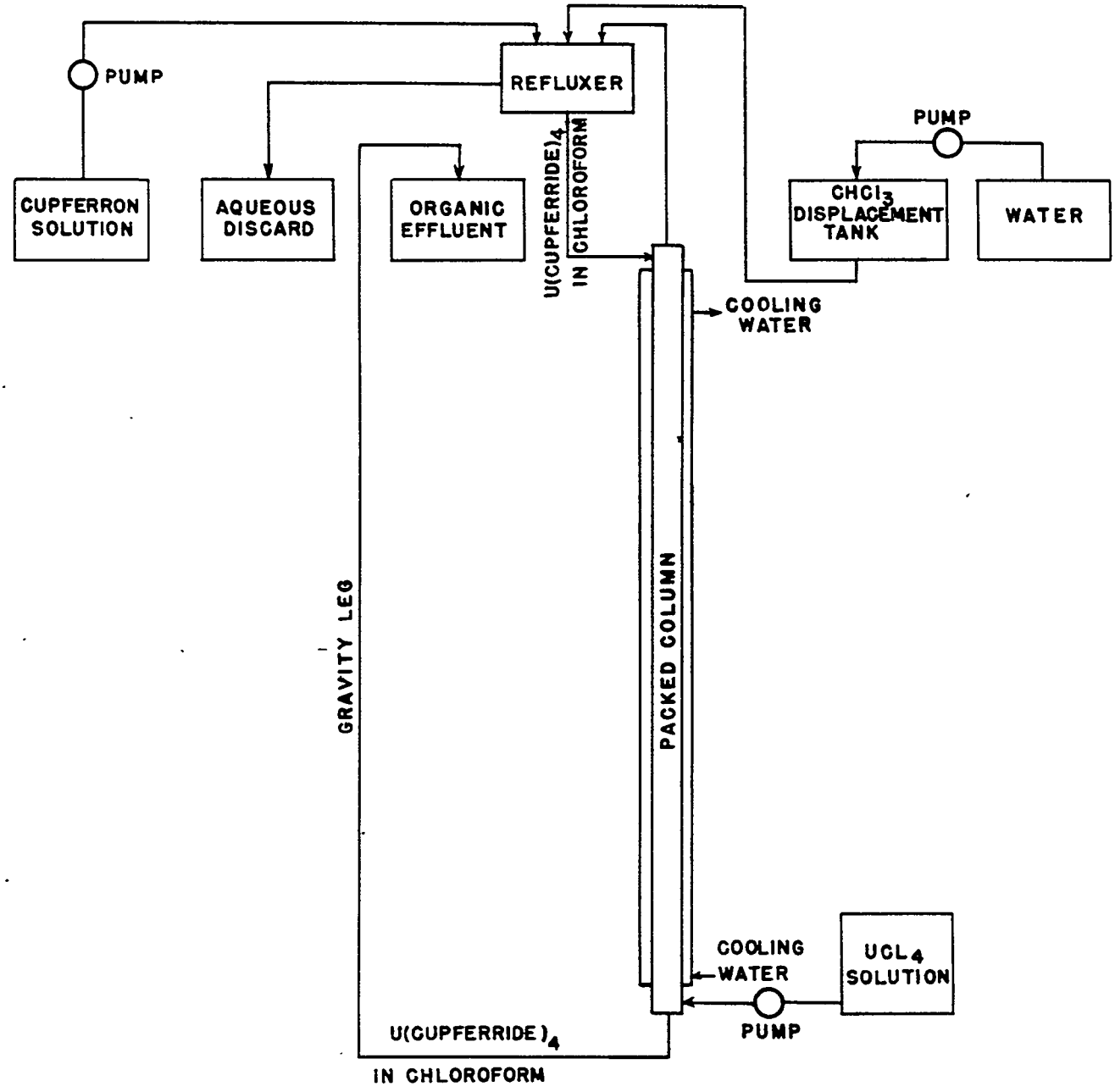


FIGURE 6- FLOW DIAGRAM OF EXCHANGE COLUMN

Final Column Run

A final sixteen-hour column run was made using 12 grams of $NaSO_2 \cdot CH_2OH \cdot 2H_2O$ per liter in the UCl_4 feed solution. All other conditions were the same as those for the last previous run. The variable speed cupferron pump was used to feed the refluxer. Losses at the top of the column were less than those previously experienced, but they were still too high to allow any enrichment. Losses were thought to be due to incomplete extraction in this case rather than oxidation. As stated earlier, the presence of the reducing agent made the extraction less efficient; a larger excess of cupferron was necessary to attain complete conversion. Of course, an increase in cupferron led to decomposition which would have caused a shutdown had the cupferron rate not been reduced. It was not possible to establish a cupferron rate slow enough to avoid decomposition and yet rapid enough to get complete extraction.

Horizontal Stirred Column Experiments

Some laboratory tests were made on horizontal stirred columns of several designs. Mixing at each stage was attained by means of mechanical stirring in vertical tube chambers. Connections between chambers needed to be such that counter flow could be attained. Both horizontal connecting tubes and inclined tubes were tried. Neither afforded steady counter flow. The best system devised was one in which each stirring chamber was followed by a settling tube. The two phases were thus separated and passed in opposite directions to their next respective stage. A sketch of this system is shown in Figure 7.

Some tracer experiments were made in order to determine the efficiency in terms of number of stages afforded by a given number of mixers. A series of six chambers was used. Uranium enriched in U^{235} was fed in one end as aqueous UCl_4 solution. Depleted uranium was fed to the other end as U(cupferride)$_4$ in $CHCl_3$ solution. Samples were taken of both phases at inlet and outlet ends. Uranium analysis and alpha count were made on each sample. The activities were then expressed in alpha counts per minute per microgram uranium in order to determine the amount of exchange that took place in the six chambers. Table 11 shows the changes in activities in the organic and aqueous phases for flow rates of approximately nine cc per minute in both phases.

Table 11

Sample	U Concentration (μ/ml)	Activity (counts/min/μ)
Aqueous (in)	167	19.9
Aqueous (out)	213	1.9
Organic (in)	198	0.5
Organic (out)	187	11.6

The concentration data showed that a transfer of material took place from organic to aqueous phase. However, no balance could be made with respect to concentration or activity. This was probably due to some inaccuracy in analytical method. Qualitatively it appeared that more exchange took place than would have occurred in a packed column of similar volume. If work is resumed using some other exchange system, it should be of advantage to study further horizontal stirring type apparatus.

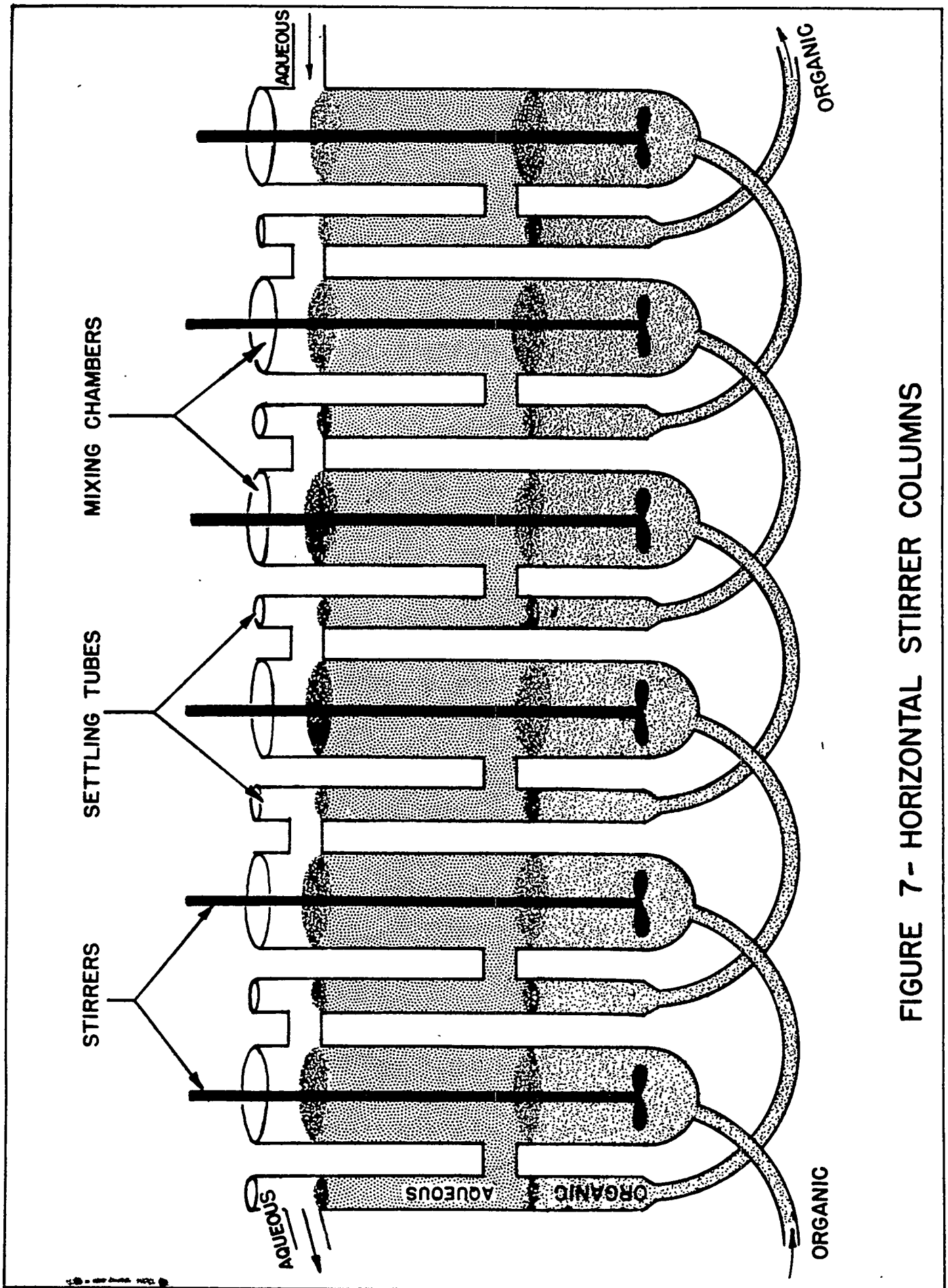


FIGURE 7- HORIZONTAL STIRRER COLUMNS

DISCUSSION OF RESULTS

The main conclusion to be drawn from this work is that the U^{+4}-U(cupferride)$_4$ system does not lend itself practically to continuous column operation. No reflux system using cupferron could be made practical due to the solubility of the acid complex in $CHCl_3$. Oxidation of U^{+4} was not effectively eliminated without further hindering the extraction at the top of the column. The oxidation problem might have been solved by the use of a more suitable reducing agent, but the system would still not be suitable for long operation because of the impractical method of reflux. In order for an exchange system to be workable, a complexing agent is needed that is soluble in acid solution and insoluble in the organic phase. The uranium complex must be stable and soluble in organic and insoluble in aqueous acid solution. A system involving UO_2^{+2} in the aqueous phase would be more easily handled since oxidation would not be encountered. It should, therefore, be much easier to eliminate losses at the reflux end of the column. Work is being continued in another laboratory in this department to develop such an exchange system which would be more adaptable to continuous column operation. Work on the U^{+4} – U(cupferride)$_4$ system has been abandonded, and the column apparatus has been placed in standby condition until a new exchange system can be devised.

Factors necessary to attain an economically practical process even further complicate the problem. It would be necessary to develop reflux mechanisms for both ends of the column. Also high recovery of complexing agent and organic solvent for re-use would be required. A single stage separation factor of 1.002 or larger would probably be necessary in order for any exchange process to compete economically with existing processes.

SECTION 3

ORGANIC COMPLEXING AGENTS FOR URANIUM

Because of difficulties encountered in the use of cupferron, a search was inaugurated to find organic compounds more suitable for forming inner complex compounds with tetravalent uranium for use in exchange reactions of the type

$$U^{238\,+4} + U^{235}(\text{Complex})_4 \rightleftharpoons U^{235\,+4} + U^{238}(\text{Complex})_4$$

Aqueous Organic Aqueous Organic

It is obvious that if such a system is to function properly, a number of criteria are imposed upon the $[U(\text{Complex})_4]^0$. The most important properties which the complex should possess are enumerated below:

1. The uranium complex must be stable in the presence of dilute acid solutions. This is a requisite since the complex will be in contact with a solution of U^{+4} ion. Hydrolysis of this ion takes place when the acidity falls below a pH $\cong$ 1.9. So it must always be more acid than this.
2. Uranium ion is readily oxidized so the organic should not be an oxidizing agent or tend to cause oxidation indirectly.
3. The complex of uranium must form readily and not require a large excess of reagent.
4. The complex must be bonded tightly enough to be stable and extract into the organic solvent yet it must permit an exchange of uranium to take place with the ionic form in aqueous solution.
5. The complex should not cause emulsification when the organic and aqueous phases are agitated in the presence of each other.
6. Cost of the complexing reagent should be reasonable.
7. The organic compound should be recoverable.

Since reagents have been rejected when the above requirements were not fulfilled, it is reasonable to assume some compounds were eliminated that would have shown complexing action under different conditions of acidity, solvents, etc.

Considering the requirements for a uranous complex, the most desirable class of compounds for investigation seemed to be inner complex salts, that is, metal-organic, chelate non-electrolytes. A general review of the literature on this subject has been made (16-25). Inner complex compounds are insoluble in water, soluble in non-polar solvents, and usually very stable. The uranous form of uranium has a coordination number of eight (26) and a principal valence of four, that is the coordination number is just twice the principal valence. Therefore to form an inner complex compound $[U(\text{organic})_4]^0$ it is necessary to have an organic compound containing one coordinating group and one acidic group (16). Using four of these molecules to complex the U^{+4}, the uranium is "satisfied" and has no charge. The same results may be obtained by organic molecules containing two coordinating groups and two acidic groups; then only two molecules are necessary to complex U^{+4}. Bidentate compounds are much more numerous than quadridentate, and so quadridentate compounds were not investigated.

Acidic groups in organic compounds are hydroxyl (OH), mercapto (SH), and imino (=NH). These groups are either attached directly to the hydrocarbon nucleus or separated by other groups such as C=O, N, NO, SO, SO_2, As, and AsO which give the carboxylic acid (COOH) the oxime or enolic form of the nitroso group (N-OH), nitroxyl or enolic form of the nitro group (NO-OH), sulfinic acids (SO-OH), sulfonic acids (SO_2-OH), arsinic ($As(OH)_2$), arsonic ($AsO(OH)_2$); the monothiocarboxylic group (COSH), and dithiocarboxylic group (CSSH); the imide group ($(CO)_2NH$). Other salt forming groups are amines and substituted amines.

The common coordinating groups are primary amines ($-NH_2$), secondary amines (-NRH), tertiary amines ($-NR_2$), cyclic tertiary amines (=N-), carbonyls (C=O), thiocarbonyls (C=S), oximes (=N-OH), nitroso groups (-NO), nitro groups ($-NO_2$), alcoholic hydroxyls (OH) and thioethers (-S-). Also, nitrogen atoms and double bond carbon atoms coordinate with metals.

Organic compounds having one acidic group and one coordinating group in the 1,2; 1,3; 2,3; 2,4; etc. positions in aliphatic compounds, and in the ortho position in aromatic compounds were investigated because inner complex compounds like organic cyclic compounds usually have five or six atoms in the ring. This is in accordance with the Baeyer strain theory.

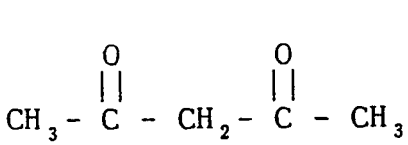
Many organic compounds were tested to determine whether or not they would react with U^{+4} and be extracted in a non-polar solvent. Chloroform and butyl acetate were chosen for extracting since they represent most water immisible solvents. Although of less interest in our work, uranyl ion was also tested in many cases for possible reaction and extraction.

A simple procedure for testing was adopted. The uranium concentration was 0.1g U in 5 ml. water. The organic to uranium ratio was five to one for uranous, and three to one for uranyl ion. The organic was weighed into a test-tube, and four ml. water added. One ml. uranium solution containing 0.1g U was added and mixed thoroughly. Any color or precipitation reaction was noted. Five ml. of one of the solvents was added and the two phases shaken together. Any extraction was noted. This was repeated using the other solvent. Four tests were made with each organic; two with uranous, and two with uranyl ion. A table of results is given in Appendix F.

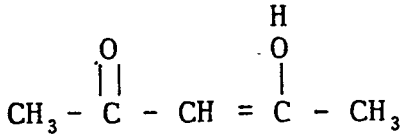
The general plan of evaluation of an organic has been as follows: First, qualitative tests to find whether an extractable complex is formed. Second, if positive tests were obtained, a more detailed examination of the extraction characteristics is made, studying such variables as acid, ratio of complexing agent to uranium, solvent, etc. Third, an "exchange" run comparable to that made with cupferron and described in Appendix B is carried out. If no exchange takes place, the organic reagent must be eliminated. Finally, if a reagent is found which possesses enough desirable characteristics, batch runs such as those described in this report will be carried out.

The compounds discussed below are those which have shown some possibilities and therefore required evaluation. Work is not complete on all these compounds.

Acetyl Acetone (2,4 Pentanedione)

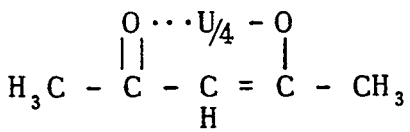


keto



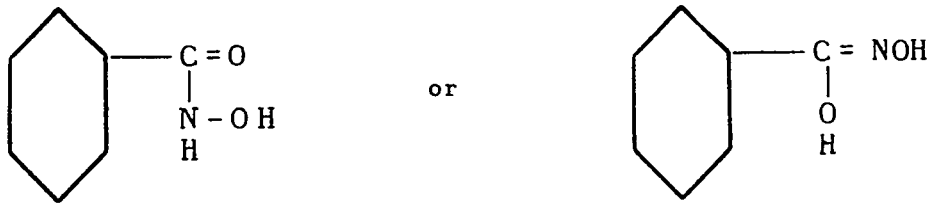
enol

Uranous acetylacetonate would presumably have the structure,



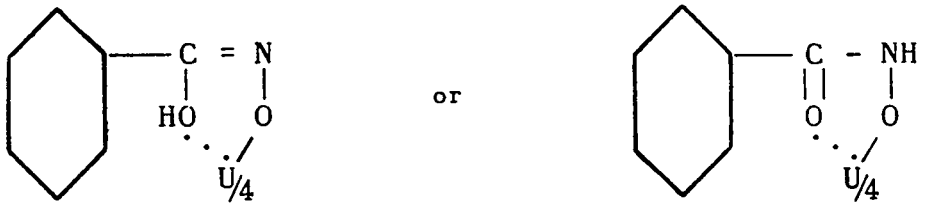
This compound may be isolated and is reasonably stable although it is doubtful whether it would undergo distillation as many other metal acetylacetonates do.

Benzohydroxamic Acid (B.H.A.)



Benzohydroxamic acid warrented investigation due to the structural similarity between this compound and cupferron, a well known reagent for tetravalent uranium. It was found that B.H.A. precipitates either U^{+4} or UO_2^{+2} from neutral solution. Uranous benzohydroxamate, an amorphous grey compound, is readily soluble in ethyl benzoate, benzaldehyde, and alcohols. Uranyl benzohydroxamate precipitates as an orange-red crystalline compound which is insoluble in all organics tested with the exception of ethyl and methyl alcohol; it is not readily soluble in these.

The structure of the uranous complex might be



The uranyl complex would be similar but would require two moles of complex per mole of uranyl ion.

Extraction data for uranous benzohydroxamate from aqueous solution using ethyl benzoate as the solvent are given in Table 12.

TABLE 12

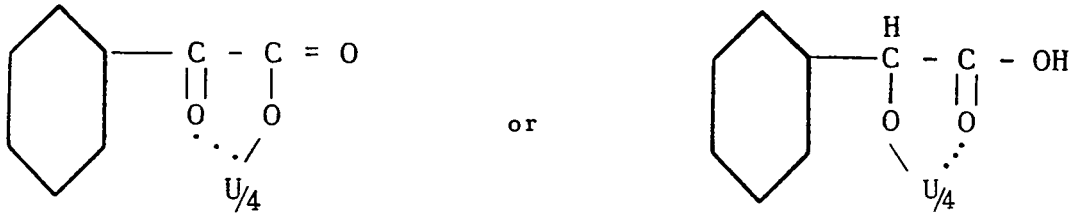
EXTRACTION OF $U(BHA)_4$ BY ETHYL BENZOATE

pH	Conc. U in Aqueous Layer Before Extraction	Mole Ratio $\frac{BHA}{U^4}$	%U Extracted (one pass)
.32	2.6%	2.5	15.5
.54	2.6%	2.5	38.1
.72	2.6%	2.5	47.5
.82	2.6%	2.5	64.2

The rate of exchange between the benzohydroxamic acid complex and the uranous ion is about the same as found using cupferron. (See Appendix B)

Benzoylformic Acid (B.F.A.) Phenylglyoxylic Acid)

This compound forms a very stable and easily extracted complex with uranous ion. Presumably the structure of the complex is



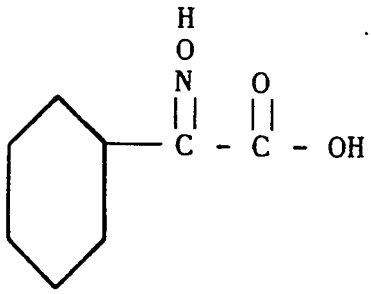
Extraction data on this compound appear in Table 13.

TABLE 13.

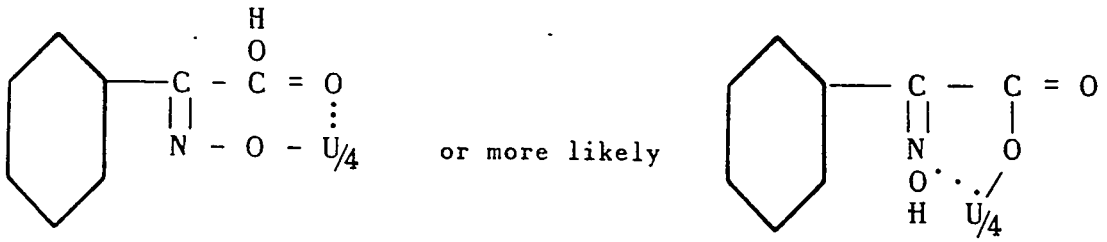
EXTRACTION OF URANOUS BENZOYL FORMATE BY $CHCl_3$

pH	Conc. of U^4 Before Extraction	Mole Ratio $\frac{\text{B.F.A.}}{U^4}$	% Extraction (one pass)
.5	3.8%	2.5	43.5
.54	3.8%	2.5	49.4
.6	3.8%	2.5	59.4

Benzoylformic Acid Oxime

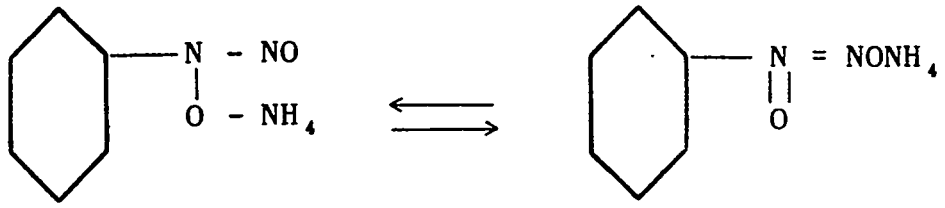


This compound complexes U^{+4} as

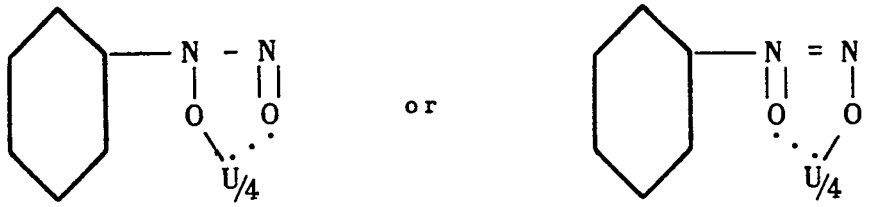


The complex is not extracted by chloroform due to the formation of an emulsion. Other solvents may possibly be used to advantage although none have been tried.

Cupferron (Ammonium salt of Phenyl Nitroso Hydroxylamine)



Cupferron, a well known analytical reagent, forms a water insoluble tan precipitate with tetravalent uranium ion. The complex is believed to exist in one or both of the tautomeric forms



and displays the properties of true inner complex as indicated by its solubility in non polar solvents.

Extraction data for uranous cupferride in two solvents are given in Tables 14 and 15.

TABLE 14

EXTRACTION OF URANOUS CUPFERRIDE BY CHLOROFORM

HCl Conc.	Conc. U Before Extraction	Mole-Ratio $\frac{\text{Cupferron}}{U^{+4}}$	% Extraction (one Pass)
1N	3%	2.0	32%
1N	3	2.6	53
1N	3	3.3	76
1N	3	4.2	97
1N	3	5.0	100

TABLE 15

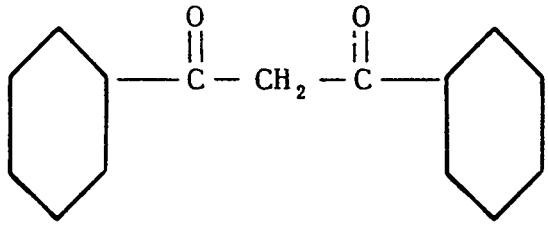
EXTRACTION OF URANOUS CUPFERRIDE BY BUTYL ACETATE

Conc. of HCl	Conc. U^{+4} Before Extraction	Mole Ratio $\frac{\text{Cupferron}}{U^{+4}}$	% Extraction (one pass)
1N	1.3%	2.0	28.9%
1N	1.3	2.5	46.0
1N	1.3	3.0	64.3
1N	1.3	3.5	82.4

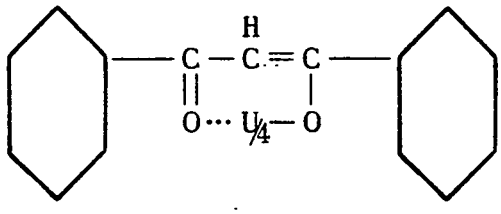
It is significant that of all the complexing agents tested with U^{+4} only the cupferride complex is stable toward acid. Solutions up to 3N HCl have been used successfully with no apparent effect on the extraction of the uranous complex. Exchange data are given in Appendix B.

Uranous cupferride in choloroform solution is rather unstable. The complex apparently oxidizes with the subsequent precipitation of uranyl cupferride. The uranous complex is somewhat more stable in Butyl acetate and other solvents.

Dibenzoyl Methane



The uranous complex formed with dibenzoyl methane would have the structure

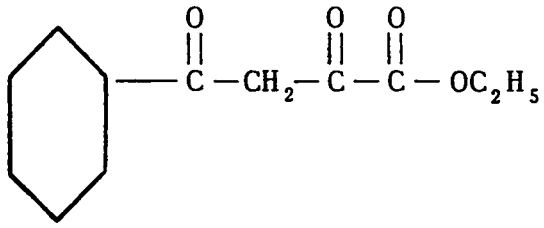


which resembles acetylacetone except phenyl groups are substituted in place of methyl groups.

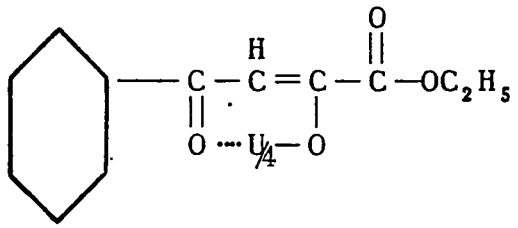
Using a 2.5 mole ratio of dibenzoyl methane an extraction of 19.8% uranium was obtained at a pH = 1.5 using chloroform.

No exchange experiment was made with this compound.

Ethyl Benzoylpyruvate (E.B.P.)



This compound reacts with uranium in aqueous solution forming an extractable complex. Uranium exchanged between this complex and U^{+4} ion at a rate too slow for our needs. Generally the properties were similiar to 2,4 pentanedione.



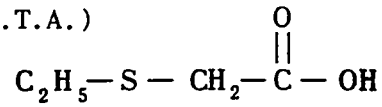
An extraction study is summarized in Table 16.

TABLE 16

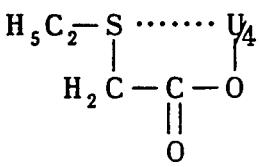
EXTRACTION OF E.B.P. COMPLEX OF U^{+4} BY $CHCl_3$

pH	Conc. U Before Extraction	Mole Ratio $\frac{\text{E.B.P.}}{\text{U}}$	% Ext. ($CHCl_3$) (one pass)
1.3	2.4%	4	16.1%
1.6	2.4	4	50.9
1.8	2.4	4	Emulsion
2.0	2.4	4	Emulsion

Ethyl Thioglycolic Acid (E.T.A.)



Uranous ions form a rather weak complex with this acid. The structure of the complex probably is



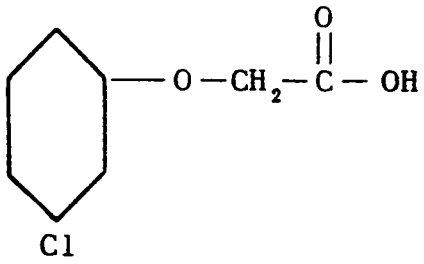
The reagent forms a white-green precipitate with uranous ions which can be extracted into chloroform to give a light green solution. Here again the complex is not stable in the presence of acid, a large excess being required to produce any degree of extraction from slightly acid solutions. The data in Table 17 bring this fact out clearly. The complex allows exchange of uranium but at a much slower rate than cupferron.

TABLE 17

EXTRACTION OF E.T.A. COMPLEX OF U BY CHLOROFORM

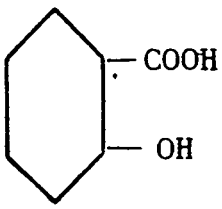
pH	Conc. U Before Extraction	Mole Ratio $\frac{\text{E:T.A.}}{\text{U}}$	% Extraction (one pass)
1.2	3.79%	9	24.8
1.2	3.79	12	39.8
1.2	3.79	15	45.1
1.2	3.79	18	50.7

p-Chlorophenoxyacetic Acid

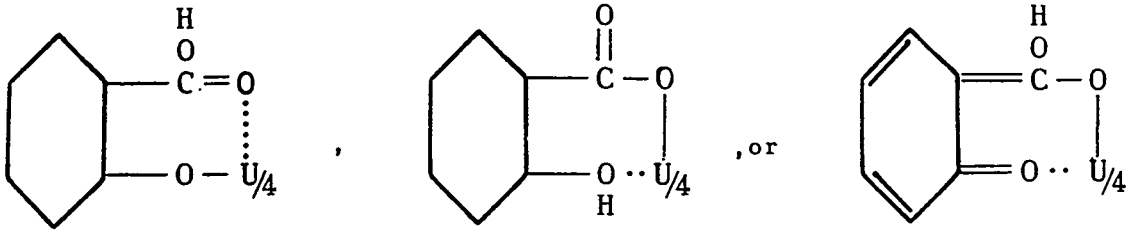


From visual observations the uranous complex with p-chlorophenoxyacetic acid is much like salicylic acid complex. No further work has been done on it. A chelate structure for this compound is not obvious. The uranous complex is extracted by chloroform.

Salicylic Acid



The uranous complex of salicylic acid probably exists in one of these forms



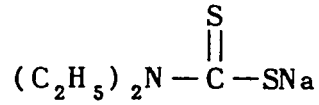
Salicylic acid because of its low solubility in water will not complex uranous ion in aqueous solutions. The sodium salt will form a white-green precipitate with uranous ions; this can be extracted with butyl acetate to give a light green solution. Salicylic acid will complex uranous ions and be extracted by chloroform if ethyl or methyl alcohol is added. The uranous salicylate complex is more sensitive to acid than cupferron; although it extracts at a pH of 2 using sodium salicylate, there is no exchange of uranium atoms, so no further study has been made with salicylic acid. There may be a slight possibility of exchange using alcohol and salicylic acid.

TABLE 18

EXTRACTION OF URANOUS SALICYLATE BY BUTYL ACETATE

Moles Ratio $\frac{\text{NaSal}}{\text{U}}$	pH Before Extraction	pH After Extraction	% Extracted (one pass)
6	.5	.9	27%
6	1.0	1.3	43
6	1.7	2.7	76
6	2.0	3.3	86

Sodium Diethyldithiocarbamate



Both uranous and uranyl ions react with this reagent. Uranous ions are precipitated and this precipitate is soluble in chloroform. Uranyl ions form a red precipitate which is soluble in chloroform. The structure of the complex may be

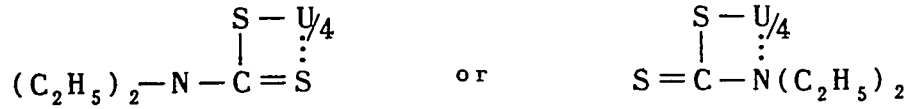
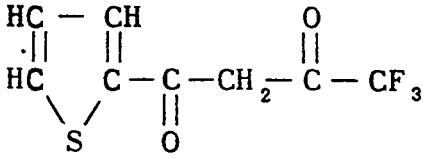


TABLE 19

EXTRACTION OF URANOUS DIETHYL DITHIOCARBAMATE BY CHLOROFORM

pH	U Conc. Before Extraction %	Mole Ratio Complex/U^{+4}	% U Extracted (one pass)
.25	3.6	2.5	5.8
.9	3.6	2.5	30
1.0	3.6	2.5	36
1.5	3.6	2.5	47

Thenoyltrifluoroacetone (T.T.A.)



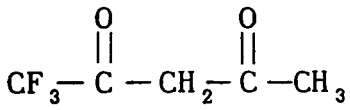
A sample of this compound was recently obtained from the University of California. Preliminary work with the $U(TTA)_4$ complex shows it may be extracted from aqueous solution by butyl acetate but chloroform does not work well. Extraction data are presented in Table 20.

TABLE 20

EXTRACTION OF URANOUS TRIFLUOROACETONATE BY BUTYLACETATE

pH	U Conc. Before Extraction %	Mole Ratio Complex/U^{+4}	% U Extracted (BuAc) (one pass)
1.05	1.9	1	12
1.05	1.9	2	26
1.05	1.9	3	36
1.05	1.9	4	48
1.05	1.9	5	59

Trifluoroacetonate (T.F.A.)



The uranous complex with this compound is analogous to that of acetylacetone although somewhat more stable in the presence of acids. Results of an extraction study are summed up in Table 21.

TABLE 21

EXTRACTION OF URANOUS TRIFLUOROACETONATE BY $CHCl_3$

pH	U Conc. Before Extraction %	Mole Ratio $\frac{TFA}{U}$	% U Extraction (one pass)
1.3	3.6	3.6	40.5
1.46	3.6	3.6	49.5
1.5	3.6	3.6	52.1

As in the case of other β diketone complexes of uranous ion, the rate of exchange was very slow.

SECTION 4

EXCHANGE OF URANIUM BETWEEN U^{+4} AND UO_2^{+2}

IN DILUTE ACID SOLUTION

In connection with other work it was desired to know whether uranium atoms exchange between the tetravalent, U^{+4}, and the uranyl, UO_2^{+2}, ionic states. Previous work by others (27,28) had given conflicting information so the question was taken up as a separate problem. The present investigation demonstrated that under certain conditions a fairly rapid interchange can be observed. A preliminary report (29) of this work was made at the October, 1947, Information Meeting held at Clinton Laboratories in Oak Ridge. Others have since observed the same exchange (30). The present report gives the complete experimental data which were not included in the original document (29).

The mode of attack was a modified tracer technique. The exchange reaction may be represented by the simple equation

$$\overset{*}{U}O_2^{+2} + U^{+4} \rightleftharpoons \overset{*}{U}^{+4} + UO_2^{+2}$$

with the unstarred uranium representing almost pure U^{238} and therefore uranium of low alpha activity. The $\overset{*}{U}$ is enhanced in U^{235} and U^{234} and has an alpha activity approximately fifty times that of the U^{238}.

The mathematical expression of the rate process may be given by the equation below. The complete derivation is given in Appendix G.

$$k = \frac{1}{t(A+B)} \ln \frac{A(B+BR)}{B(A-BR)}$$

t = time in minutes
A = wt. (γ) uranium as $\overset{*}{U}O_2^{+2}$ at t = 0
B = wt. (γ) uranium as U^{+4} at t = 0
$R = \frac{\overset{*}{U}^{+4}}{U^{+4}}$ at time = t

Quantities A, B, and t are all known. R is determined by solving simultaneous equations involving the weight and activity (alpha counts/min/microgram) of the tetravalent uranium in the system at time t (see Appendix H).

It should be pointed out that the above rate equation is not in the customary form, but has been used because of convenience. A and B are actually the micrograms of $\overset{*}{U}O_2^{+2}$ or U^{+4} in one fiftieth of the 20 ml systems which will be described shortly. Another value of the reaction rate constant, namely k', has been included in tables 22, 23, 24; k' was obtained by substituting moles per liter for A and B and t in seconds.

Three factors which were felt would affect the rate of exchange were investigated; these are discussed below:

Effect of Hydrogen Ion Concentration

Systems were made up by taking 2.00 ml of uranous chloride (12.5 mg U), solution, 2.00 ml of uranyl chloride solution (12.5 mg U), the proper amount of hydrochloric acid to give the desired pH, and making up to 20.00 ml. The pH of this system was measured with a Beckman laboratory pH meter.

From the above system a 2.00 ml aliquot was withdrawn to determine the initial U^{+4} and UO_2^{+2} (A and B) concentrations. This step was found necessary because the U^{+4} stock solution changed slightly in U^{+4} concentration from day to day due to the oxidation U^{+4} to UO_2^{+2}.

Aliquots (2.00 ml) were withdrawn from the remainder of the system at various noted times (t), transferred to a small separatory funnel, chilled, and a cupferron chloroform extraction of the tetravalent uranium made.

The chloroform solution of the uranous cupferride was diluted to 10.0 ml in a volumetric flask. From this, 2.00 ml aliquots were withdrawn for plating and counting (the count of these samples is recorded in Table 22). Further aliquots (2.00 ml) of the chloroform solution were used to determine colorimetrically the uranium present (this quantity is found in the "γU" column of Table 22).

The above determinations make it possible to compute R and thence $\frac{A(B+BR)}{B(A-BR)}$ and k.

A plot of $\frac{A(B+BR)}{B(A-BR)}$ for various values of pH versus time is given in Figure 1, Appendix J.

When the average value of the reaction rate constant, k at 28°C, is plotted against pH; Figure 2, Appendix J; the fact is revealed that the rate constant varies inversely with the hydrogen ion concentration. If the pH is as great as 2, hydrolysis of the tetravalent uranium takes place.

Effect of Temperature

The variation of the rate of the reaction with temperature was studied in the range of 23°C to 64°C. Systems used in this work were prepared in the same manner described earlier in the report. The pH in these runs was held at 1.0 and the temperature varied from run to run.

A water bath with a mercury thermoregulator was used to control the temperature. The data obtained from the experimental results and subsequent calculations are presented in Table 23.

Plots of these data, Figures 3 and 4 in Appendix J, reveal that the log of the rate constant is inversely proportional to the absolute temperature.

Taking the average rate constants for two different temperatures, a calculation of the Energy of Activation may be made

$$T_1 = 312^\circ;\ k_1 = 2.58 \times 10^{-6}$$

$$T_2 = 317^\circ;\ k_2 = 5.26 \times 10^{-6}$$

$$\log k_2/k_1 = Q(T_2 - T_1)/2.303\ RT_1T_2$$

$$\log \frac{5.26 \times 10^{-6}}{2.58 \times 10^{-6}} = Q(317 - 312)/2.303 \times 2 \times 312 \times 317$$

$$\log 2.03 = Q\ \frac{5}{4.56 \times 10^5}$$

$$.308 = Q\ 1.1 \times 10^{-5}$$

$$28{,}000 \text{ calories/mole} = Q$$

TABLE 22

Effect of pH on Rate of Exchange

t = 28°

Run No.	pH	t (min)	A(γ)	B(γ)	c/m of Aliquot	γ U in Aliquot	R	$\frac{A(B+BR)}{B(A-BR)}$	k	k (average)	k′ (sec^{-1})
IV	1.1	0	312	188							
IV		85			263	165	.08	1.13	2.9×10^{-6}		
IV		218			448	135	.21	1.39	3.0×10^{-6}	3.1×10^{-6}	4.9×10^{-3}
IV		310			537	118	.33	1.66	3.3×10^{-6}		
III	1.3	0	350	150							
III		5			139	150	.04	1.05	19.6×10^{-6}		
III		16			286	145	.12	1.18	20.7×10^{-6}	18.8×10^{-6}	29.8×10^{-3}
III		40			488	138	.27	1.43	18.0×10^{-6}		
III		100			785	123	.67	2.33	17.0×10^{-6}		
VIII	1.9	0	345	155							
VIII		4			268	155	.10	1.15	69.0×10^{-6}		
VIII		31			1050	154	.73	2.60	62.2×10^{-6}	62.9×10^{-6}	99.8×10^{-3}
VIII		63			1349	153	1.35	6.00	57.6×10^{-6}		

NOTE: A and B in Table 22 are actually only one-fiftieth of the amount of tetravalent and uranyl ion present in the original system. It is convenient to use these values since the activity and colorimetric determinations also represent one-fiftieth of the original system.

TABLE 23

Effect of Temperature on the Rate of Exchange at pH 1.0

Run No.	Temp. (°C)	t (min)	A(γ)	B(γ)	c/m of Aliquot	γ U in Aliquot	R	$\frac{A(B+BR)}{B(A-BR)}$	k	k (average)	k′
1	23	1131	344	156	122	156	.026	1.04	6.6×10^{-8}		
1	23	2805			106	109	.045	1.06	4.0×10^{-8}	5.3×10^{-8}	8.4×10^{-8}
2	39	15	243	257	148	257	.008	1.02	2.3×10^{-6}		
2		52			223	210	.039	1.07	2.5×10^{-6}		
2		96			363	207	.082	1.15	2.9×10^{-6}	2.6×10^{-6}	4.1×10^{-3}
2		154			479	205	.124	1.23	2.7×10^{-6}		
3	44	17	298	202	167	202	.025	1.04	5.0×10^{-6}		
3		53			425	243	.072	1.15	5.2×10^{-6}	5.3×10^{-6}	8.4×10^{-3}
3		101			643	216	.162	1.33	5.6×10^{-6}		
4	64	15	283	217	1072	217	.326	1.77	7.6×10^{-5}		
4		34			1726	207	.778	4.06	8.2×10^{-5}	7.9×10^{-5}	12.5×10^{-2}

TABLE 24

Effect of Light on Rate of Exchange

Run No	Ex-posure	pH	t (min)	A (γ U)	B (γ U)	c/m of Aliquot	γ U in Aliquot	R	$\frac{A(B+BR)}{B(A-BR)}$	k	k (average)	k′
L-1	U.V.	1.08	0	325	175							
		1.08	5			76	162	.004	1.004	1.6×10^{-6}		
		1.08	71			131	170	.024	1.040	1.0×10^{-6}		
		1.08	170			226	145	.079	1.090	1.0×10^{-6}	1.1×10^{-6}	1.74×10^{-3}
		1.08	229			229	136	.088	1.120	0.9×10^{-6}		
L-2	U.V.	1.52	0	268	232							
		1.52	45			903	243	.200	1.630	21.0×10^{-6}		
		1.52	105			1135	203	.350	3.100	22.0×10^{-6}	21.3×10^{-6}	33.8×10^{-3}
		1.52	171			943	163	.390	6.200	21.0×10^{-6}		
D-1	Dark	1.08	0	325	175							
		1.08	42			81	163	.010	1.020	0.9×10^{-6}		
		1.08	97			131	147	.030	1.050	1.0×10^{-6}	1.0×10^{-6}	1.6×10^{-3}
		1.08	194			171	102	.090	1.110	1.0×10^{-6}		
D-2	Dark	1.20	0	360	140							
		1.20	6			59	173	.008	1.002	0.6×10^{-6}		
		1.20	80			96	160	.014	1.050	1.1×10^{-6}	0.9×10^{-6}	1.4×10^{-3}
		1.20	148			109	145	.011	1.080	1.0×10^{-6}		
D-3	Dark	1.35	0	327	173							
		1.35	4			73	180	.003	1.003	1.5×10^{-6}		
		1.35	38			146	175	.028	1.060	3.1×10^{-6}	2.6×10^{-6}	4.1×10^{-3}
		1.35	85			294	170	.093	1.130	2.9×10^{-6}		
		1.35	144			343	163	.120	1.230	2.8×10^{-6}		
D-4	Dark	1.52	0	319	181							
		1.52	6			148	230	.019	1.030	9.8×10^{-6}		
		1.52	61			435	155	.176	1.280	8.1×10^{-6}	8.7×10^{-6}	13.8×10^{-3}
		1.52	125			755	132	.470	1.700	8.5×10^{-6}		
		1.52	199			347	61	.550	2.250	8.2×10^{-6}		
D-5	Dark	1.64	0	360	140							
		1.64	5			157	230	.047	1.030	11.8×10^{-6}		
		1.64	33			573	213	.190	1.210	11.5×10^{-6}	11.4×10^{-6}	18.1×10^{-3}
		1.64	85			749	204	.290	1.61	11.2×10^{-6}		
		1.64	174			473	194	.170	2.650	11.2×10^{-6}		

Effect of Ultraviolet Light

It had been reported by Heal (31) that the presence of ultraviolet light increases the concentration of a pentavalent uranium ion. Since the U^{+4} - UO_2^{+2} exchange process could conceivably involve the formation of an intermediate pentavalent ion, several experiments were carried out to find whether the rate of exchange could be altered by exposing the system to ultraviolet light.

To do this, systems were prepared and exposed to an ultraviolet light source while others were placed in a heavily wrapped blackened bottle. The apparatus is shown in Figure 8.

It is seen that the system exposed to the ultraviolet source was also exposed to the normal light in the room, as were all other experiments so far described.

The intensity of the ultraviolet light had been previously checked (see Appendix K) and found to be 14×10^{15} quanta per second in a system physically identical to that used for the exchange systems. Using this value for the ultraviolet radiation, it was determined that an exposure time on the order of an hour would be sufficient for complete activation of the uranium ions in the system.

The results obtained from these runs are presented in Table 24.

The experimental data have been plotted in Figure 5 and Figure 6 of Appendix J. Figure 6 shows that the rate of the exchange reaction is appreciably slower in the dark than in systems exposed to ultraviolet light. If the exchange rate of the ultraviolet system is compared to its counterpart in normal daylight as in Figure 6, the difference in rate is seemingly negligible. The data do not allow any conclusion to be drawn regarding the effect of the ultraviolet source in the absence of other light.

DISCUSSION

Although the effect of several variables on the rate of exchange of uranium between the tetravalent and hexavalent states has been studied, no explanation of the mechanism of this exchange is being presented here. However, the results do provide a basis for certain speculations. It seems significant that the pH range in which the exchange is most rapid is also the range in which hydrolysis of U^{+4} with ultimate precipitation of colloidal UO_2 is favored. The extreme hydrolyzed form of the tetravalent uranium, $U(OH)_4$, would of course be favored with rising pH. It also seems possible that the hydrated form of the hexavalent uranium, $[UO_2(OH_2)_2]^{+2}$, might tend to become $[U(OH)_4]^{+2}$ with rising pH. A simple electron transfer between these two similar species does not seem unlikely.

By the use of oxygen isotopes, Crandall (34) was able to clarify the identity of the oxygen atoms in the UO_2^{+2} ion in solutions .1 to .65 N in HCl. It would seem that similar studies in the pH range of 1 to 1.9 would add considerably to an understanding of the exchange mechanism.

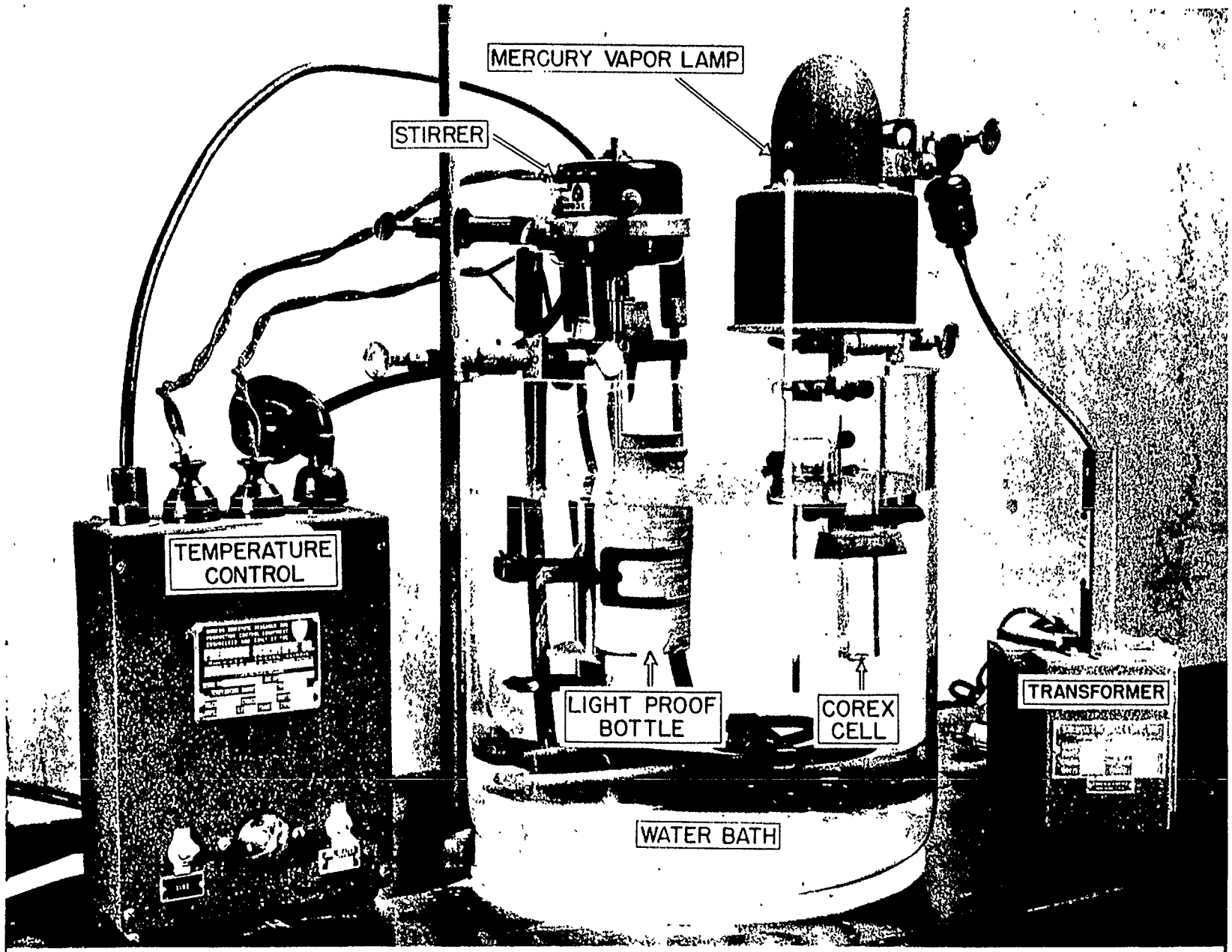


FIGURE 8 - ULTRAVIOLET EXPOSURE APPARATUS

SUMMARY

A brief discussion of the general theoretical background of chemical methods for isotope enrichments has been given.

The enrichment of uranium isotopes was achieved by making use of an exchange reaction involving the interchange of uranium between the inner complex, uranous cupferride, dissolved in chloroform, and uranous ion in aqueous solution. Both batch and continuous (column) methods were used. Batch experiments showed some separation, but continuous column work was unsuccessful because of the oxidation of the organic complexing agent and the relatively slow reaction rate which greatly lengthened the height of one theoretical stage in the column.

Extensive research designed to find a more suitable organic compound which will form inner complex compounds with uranium ions is presented. Although many compounds were found which show some promise, none has been found to date which has properties sufficiently desirable to warrant large scale experimentation. More than 175 compounds of promising structure have been investigated.

It has been demonstrated that some separation of the isotopes of uranium can be effected by equilibrating a mixture of uranous and uranyl ions at the proper pH, followed by a selective precipitation of the uranous ions. A remarkable feature of this study has been the demonstration that the uranous ion which has previously been thought of as having a relatively simple structure in solution (U^{+4}) appears to be more complex than the uranyl ion (UO_2^{+2}) since it has been shown that the isotope U^{235} concentrates in the uranyl ion which, according to present accepted theory, must be the less complex form.

Future work designed to improve the separation factors and possibly to combine in some convenient manner the two reactions already tested has been outlined.

Although it appears that considerable research may be necessary before a practical method of utilizing chemical exchange reactions will be uncovered, the present work is significant in demonstrating that the chemical separation method might offer unusual attractiveness.

APPENDIX A

Calculation of Equilibrium Constant for the $U^{+4} \longleftrightarrow UO_2^{+2}$ Exchange Reaction.

The calculation of equilibrium constants for an isotope exchange reaction may be summarized briefly. Such an equilibrium constant is directly obtainable from the free energy-change in the reaction. The free energy of any substance is given by its partition function, Q, from the relation

$$F = -RT \ln Q$$

The partition function expresses the probability of each possible energy state in the molecule. It is obvious that the free energy of a substance may be obtained by summing the free energies of each of the molecules present. Likewise it is given by summing the energies obtained by multiplying the number of molecules present of a given energy, by the amount of that energy. Equally well, it may be considered to be the result of multiplying the number of molecules present by the chance (probability) that each of them may have any of the particular amounts of energy that are possible, and summing over all the probabilities. Since we are concerned with one mole of compound, all that remains is the probability sum, the partition function.

Since in a reaction we are concerned with ΔF, the difference between the free energies of reactants and products, we may immediately write

$$F_2 - F_1 = \Delta F = -RT \ln \frac{Q_2}{Q_1} = -RT \ln K, \text{ where } K = \frac{Q_2}{Q_1}$$

The partition function expresses all energy states of the molecule, but it can be shown that in an exchange reaction all except vibrational states are the same for each isotope. Therefore since a ratio is involved, all but the vibrational states cancel out, and the calculation reduces to the estimation of the differences in vibrational levels to be found in the two isotopic molecules. A knowledge of the frequencies of the vibrational levels in all the molecules involved may be obtained in several ways, and leads directly to the calculation of the equilibrium constant. If the necessary frequencies have not been measured, they may occasionally be estimated with reasonable accuracy.

If one assumes that uranous and uranyl ion exist in aqueous solution simply as U^{+4} and UO_2^{+2} the isotopic exchange reaction between the ionic species may be represented by the equation:

$$U^{238\ +4} + UO_2^{235\ +2} \rightleftharpoons U^{235\ +4} + UO_2^{238\ +2}$$

The methods of Bigeleisen and Mayer (3) may be applied to evaluate the equilibrium constant of this exchange reaction. Calculations of the separative effect by the "long" method and "short" method are carried out below. Essentially the same result is obtained by either method.

Long Method of Calculation of Separative Effect:

The separative effect, S/S'f, for an isotopic exchange reaction may be calculated from the function

$$S/S'f = 1 + \Sigma_i(\tfrac{1}{2} - 1/u_i + 1/e^{ui} - 1)\Delta u_i$$

where S/S' = ratio of symetry numbers of the molecule = 1
$u_i = hcw_i/kT$
h = Planck's Constant = 6.6×10^{-27}
c = velocity of light = 3×10^{10} cm./sec.
w_i = vibration frequency in cm^{-1}
k = Boltzman constant = 1.38×10^{-16} ergs/degree
T = ^oK = 300

let

$$G_i = (\tfrac{1}{2} - 1/u_i + 1/e^{ui} - 1)$$

for the Uranyl ion at 300°K

	i=1	i=2	i=3
w_i^*	860	220	940
Δw_i^*	0	0.17	0.71
u_i	4.2197	1.5049	4.5072
Δu_i	0	0.00082	0.0034
G_i	0.27792	0.08632	0.28928
$G\Delta u_i$	0	0.00007	0.00099

$$S/S'f = 1 + \Sigma_i(G\Delta u_i) = 1 + 0.00099 + 2(0.00007)^{**}$$

$$f = 1.0011$$

*Values reported by G.H. Dieke; A-3227 (1945)
**Multiplied by 2 because w_2 is doubly degenerate

Short Method of Calculation of Separative Effect:

$$S/S'f = 1 + (\Delta Mn/\ 24MM')u^2n$$

where S/S' = ratio of symetry numbers of molecule = 1
M = mass of heavier isotope = 238
M' = mass of lighter isotope = 235
ΔM = difference in mass of isotopes
m = mass of binding atom = 16 (for UO_2^{+2})
n = number of binding atoms in molecule = 2 (for UO_2^{+2})
u = hcw/kT

h = Planck's Constant
c = velocity of light
w = vibration frequency of molecule
T = ^{o}K = 300
k = Boltzman's constant = 1.38×10^{-16} ergs/degree

for the Uranyl ion f = 1.0011

The equilibrium constant for the reaction is the ratio of the separation effect of the isotope in the complex molecule to the separation effect in the dissociated ionic form. We have assumed that there are no strong bonds and, therefore, the separation effect due to the U^{+4} state is 1.00000. Table A1 shows the equilibrium constants.

TABLE A1

Equilibrium Constants for $U^{+4} \longleftrightarrow UO_2^{+2}$ Exchange

Species	f		K	
	short	long	short	long
UO_2^{+2}	1.0011	1.0011	1.0011	1.0011
U^{+4}	1.0000*	1.0000*		

*Assuming no strong bonds

APPENDIX B

Exchange of Uranium between U^{+4} ion Aqueous Solution and $U(C_6H_5N_2O_2)_4$ in Chloroform.

If the isotopes of uranium are to be separated by a process based on an exchange reaction, it is required that there be a free interchange of the uranium atoms. In the case under consideration this exchange must take place between the U^{+4} ions in aqueous solution and uranous cupferride in chloroform.

A convenient way of checking for exchange is by the use of tracers. It is obvious that if a system is prepared in which the U^{+4} ion is represented by uranium of higher alpha activity than the uranium of the cupferride complex, and exchange does take place, there will be an increase in the alpha activity of the complexed uranium and a corresponding decrease in the U^{+4}.

An experiment utilizing this principle was carried out as follows: stock solutions equal in uranium concentration of $\overset{*}{U}^{+4}$ ($\overset{*}{U}^{+4}$ has been tagged, the alpha activity is 22 counts/min./microgram) and $\overset{\circ}{U}^{+4}$ ($\overset{\circ}{U}^{+4}$ is pure U^{238} having an alpha activity of 0.4 c/m/microgram) were made up. Equal volumes of these solutions were 50% extracted by adding 2.5 moles of cupferron per mole of uranium and a volume of chloroform equal to that of the aqueous, then agitating several minutes. The phases were then separated and 10.0 ml of the chloroform solution of $\overset{\circ}{U}(C_6H_5N_2O_2)_4$ was added to 10.0 ml of $\overset{*}{U}^{+4}$ (aqueous). This system was then agitated and aliquots were withdrawn from the water and chloroform phases at noted times for the determination of the activity of the uranium. These results are to be found in Table B-1.

TABLE B-1

Exchange of Uranium Between U^{+4} and $U(C_6H_5N_2O_2)_4$

Phase	Sample time Seconds	U in 1.0 ml Micrograms	Counts/min./ml	c/m/microgram
Aqueous	0			22.0
	30	1190	19660	16.5
	60	1260	14820	11.8
	120	1135	16100	14.2
$CHCl_3$	0			0.4
	30	1055	5850	5.5
	60	1110	9960	9.0
	120	1085	9230	8.5

These results indicate that equilibrium should be established in this system in a matter of one to two minutes. This time is adequate for the "batch" systems which were always agitated at least fifteen minutes.

APPENDIX C

Rate of exchange of Uranium Between U^{+4} and UO_2^{+2} in Dilute Acid Solution.

By the use of tracers a study of the exchange of uranium between U^{+4} and UO_2^{+2} in dilute HCl has been made and reported in detail eslewhere. It was found that if the reaction is represented as

$$\overset{\circ}{U}^{+4} + \dot{U}O_2^{+2} \underset{\longleftarrow}{\overset{k}{\longrightarrow}} \dot{U}^{+4} + \overset{\circ}{U}O_2^{+2}$$

where $\overset{\circ}{U}^{+4}$ has a low alpha activity, and $\dot{U}^{+4}$ has a high alpha activity, the reaction rate constant is represented by

$$k = \frac{1}{t(A+B)} \ln \frac{A(B+BR)}{B(A-BR)}$$

when t = time in seconds

A = Moles per liter of U as $\dot{U}O_2^{+2}$, t = 0

B = Moles per liter of U as $\overset{\circ}{U}^{+4}$, t = 0

$R = \frac{\dot{U}^{+4}}{\overset{\circ}{U}^{+4}}$ at time = t

In the case of our batch experiments the concentration of A = B, therefore, the rate equation reduces to

$$k = \frac{1}{t\ 2A} \ln \frac{(1 + R)}{(1 - R)}$$

From this equation it is seen that R approaches a value of unity as t approaches infinity. Since all values in the above equation are known with the exception of R for our systems, an extimation of the completeness of the exchange may be made by solving for R.

A typical "batch" contained 2% of uranium in the form of each ion.

$$A = \frac{20}{238} = .084 \text{ mole} \qquad 2A = .17 \text{ mole}$$

the time for standing was at least an hour, t = 60 x 60 = 3600 sec.,

the temperature was 28°C, pH = 1.5, and K = $2.1\ 10^{-2}$ (from the report Y184).

Solving for R

$$2.1 \times 10^{-2} = \frac{1}{3600 \times .17} \ln \frac{1 + R}{1 - R}$$

$$12.85 = \ln \frac{1 + R}{1 - R}$$

$$e^{12.85} = \frac{1 + R}{1 - R}$$

$$3.808 \times 10^5 (1 - R) = 1 + R$$

$$(3.808 \times 10^5 + 1) R = 3.808 \times 10^5 - 1$$

$$R = \frac{3.808 \times 10^5 - 1}{3.808 \times 10^5 - 1} \cong 1$$

This indicates sufficient time has been allowed for the systems to come to equilibrium.

APPENDIX D

Exchange of Uranium Between UO_2^{+2} and $U(C_2O_4)_2$:

In the runs which made use of the $U^{+4} \longleftrightarrow UO_2^{+2}$ exchange reaction, the U^{+4} was recovered by precipitating with oxalic acid after enough HCl had been added to make the solution 3N HCl. Other work had shown that exchange of uranium between the oxalate precipitate and UO_2^{+2} ion in a 3N HCl solution was unlikely. The possibility was checked, however, by tracer technique.

Two uranium solutions were prepared using different activities of uranium. One of these was 4% $\overset{\circ}{U}^{+4}$ in 3N HCl (α activity $\overset{\circ}{U}$ = 0.4 C/M/γ); the other was 4% $\overset{*}{U}O_2^{+2}$ in 3N HCl (α activity $\overset{*}{U}$ = 22C/M/γ). Systems were made up by combining equal aliquots (5.0 ml.) of these solutions. A precipitation of the U^{+4} was then carried out by adding a 5% excess (over theory) of oxalic acid. The precipitate in contact with the UO_2^{+2} solution was mechanically agitated for a known time at the end of which the $\overset{*}{U}(C_2O_4)_2$ was filtered off, washed, dried and ignited to U_3O_8 for weighing. The U_3O_8 was then dissolved in HNO_3 and two aliquots plated to determine the α activity. Results appear in Table D-1.

TABLE D-1

Exchange of Uranium Between $U(C_2O_4)_2$ and UO_2^{+2} in 3N HCl

System	Ml. 4% $\overset{\circ}{U}^{+4}$	Ml. 4% $\overset{*}{U}O_2^{+2}$	Wt. (g.) Oxalic Acid Added	Time (Hours)	Wt. (g.) U_3O_8 from $U(C_2O_4)_2$	Activity of U from $U(C_2O_4)_2$ C/M/γ
1	5	-	.222	1.5	.1798	.37 .40
2	5	5	.222	1.5	.1793	.40 .53
3	5	5	.222	23.5	.1798	.33 .43
4	5	5	.222	52.0	.1795	.42 .42

The uranium from the oxalate precipitate showed no increase in activity after fifty two hours. It is concluded that no exchange of uranium takes place between UO_2^{+2} and $U(C_2O_4)_2$ precipitate in 3N HCl.

APPENDIX E

STATISTICAL ANALYSIS OF ISOTOPIC EXCHANGE DATA: by W. M. Leaders

Data were obtained from experiments involving 9 stages of enrichment and depletion. Data comprise 103 analyses at various stages and all points are plotted in the graph attached (Figure 1).

Based on the following assumptions:

1. A straight line relationship will be a very close approximation to the true relationship when the given number of stages is small,

2. The initial concentration of U^{235} is known to be 0.7052%,

3. The results obtained at any given stage are distributed normally around the best line,

the data have been treated to determine the slope of the best line according to the general formula

$$y = ax + b \qquad (1)$$

where x = stage number
a = slope of the line
b = known starting concentration of U^{235} = 0.7052% = the y intercept.

The best line has the following characteristic, if the data are distributed according to assumption 3 above, namely, the sums of the squares of the deviation from the best line is a minimum. This can be expressed as follows:

$$\Sigma (y_o - y)^2 \text{ is a minimum.}$$

Substituting the calculated value of $y = ax + b$, we have

$$\Sigma (y_o - ax - b)^2 \quad \text{or}$$

$$\Sigma (y_o^2 - 2axy_o - 2by_o + 2abx + a^2x^2 + b^2) \text{ is to be minimized.}$$

In order to minimize this expression we take the first derivative with respect to the only variable, namely, a; since all other values are either known constants or obtainable from the data. Thus

$$d/da\ \Sigma (y_o^2 - 2axy_o - 2by_o + 2abx + a^2x^2 + b^2) = 0 \qquad (2)$$

or

$$\Sigma -2xy_o + \Sigma 2bx + \Sigma 2ax^2 = 0 \qquad (3)$$

Solving for "a", we have

$$a = \frac{\Sigma xy_o - \Sigma bx}{\Sigma x^2} \qquad (4)$$

in which we have "a" in terms of the data obtained from the experiment.

The result obtained indicates the best value of a = 0.000439. Therefore, the equation for the best line is:

$$y = 0.000439\,x + 0.7052 \qquad (5)$$

Having determined "a", we are now interested in the variance of "a" so that confidence interval statements concerning the true value of "a" may be made.

There are two theorems which must be used to determine the variance of "a". First: A linear combination of normal populations is a normal population, and, second: if

$$w = \sum_{i=1}^{n} c_i z_i \qquad (6)$$

then, where the z_i terms are uncorrelated

$$V(w) = \sum_{i=1}^{n} c_i^2\, V(z_i) \qquad (7)$$

where V(w) and V(z) mean the variances of the respective quantities.

From equation (4) above

$$a = \frac{\Sigma x y_o - \Sigma b x}{\Sigma x^2} \qquad (4)$$

or

$$a = \frac{\Sigma x y_o}{\Sigma x^2} - \frac{\Sigma b x}{\Sigma x^2}$$

and the variance of "a" is

$$V(a) = V\left[\frac{\Sigma x y_o}{\Sigma x^2}\right] + V\left[\frac{\Sigma b x}{\Sigma x^2}\right] \qquad (8)$$

However, since b is a constant and the x values are known absolutely, the variance of the second member of the right hand term of equation (8) is zero. Equation (8) may be written

$$V(a) = V\left[\frac{x_1 y_1 + x_2 y_2 + \cdots\cdots\cdots + x_n y_n}{x^2}\right]$$

and if we let

$$\frac{x_1}{\Sigma x^2} = c_1 \; ; \frac{x_2}{\Sigma x^2} = c_2 \; ; \cdots\cdots\cdots$$

we have

$$V(a) = V\left(\sum_{i=1}^{n} c_i y_i\right)$$

the terms of which are identical in form to equation (6). Now, therefore, from the second theorem above we know

$$V(a) = \sum_{i=1}^{n} c_i^2\, V(y)$$

but the best estimate of the variance of y is the sum of the squares of the deviations of y about the computed line divided by one less than the number of

data points, or

$$V(a) = \sum_{i=1}^{n} c_i^2 \frac{\Sigma(y_o - y)^2}{n - 1}$$

where

$$\Sigma c_i^2 = \frac{\Sigma x^2}{(\Sigma x^2)^2} = \frac{1}{\Sigma x^2}$$

therefore,

$$V(a) = \frac{\Sigma(y_o - y)^2}{\Sigma x^2 (n - 1)}$$

or

$$S^2a = \frac{\Sigma(y_o - y)^2}{\Sigma x^2 (n - 1)} \qquad (9)$$

substituting

$$y = ax + b$$

$$S^2a = \frac{\Sigma(y_o - ax - b)^2}{\Sigma x^2 (n - 1)}$$

$$S^2a = \frac{\Sigma(y_o^2 - 2axy_o - 2by_o + 2abx + a^2x^2 + b^2)}{\Sigma x^2 (n - 1)}$$

this expression still involves quantities not given in terms of the original data, namely, "a" and "a^2". However, using equation (4) we can eliminate all "a" and "a^2" terms and arrive at

$$S^2a = \frac{\Sigma y_o^2 - 2b\Sigma y_o + nb^2 - \frac{(\Sigma xy - b\Sigma x)^2}{\Sigma x^2}}{\Sigma x^2 (n - 1)} \qquad (10)$$

we thus have an equation for the variance of "a" in terms of the original data.

Making the summations indicated in equation (10) we obtain

$$S^2a = 0.052755 \times 10^{-8}$$

$$S(a) = 0.2297 \times 10^{-4}$$

$$S(a) = 0.000023$$

We now have all the values needed to make confidence interval statements concerning the slope of our line. By interpolating in the "t" tables between 60 and 120 degrees of freedom, which are given, we find for the data in hand, namely, 103 experimental points, that when

$$P = 0.05 \quad : \quad t = 1.99$$

$$P = 0.001 \quad : \quad t = 3.375$$

Thus the 95% symmetrical C.I. on "a" is

$$(0.000439 \pm 1.99(0.000023))$$

or

$$(0.000484 \; ; \; 0.000393)$$

The 99.95% one sided interval placing a minimum value on "a" is:

$$99.95\%\ \text{C.I.} \quad a > 0.000361$$

There is a simple relationship existing between α (the enrichment factor) and the slope of our line, "a", as determined above; a close approximation of this relationship is:

$$\alpha = \frac{0.7052 + a}{0.7052 - a} \qquad (11)$$

by substituting the calculated value of "a" we can determine α, or

best single value of $\alpha = 1.001246$

To determine the variance of α we proceed as follows:

$$\alpha = \frac{0.7052 + a}{0.7052 - a} \qquad (11)$$

as the first approximation of α, or

$$\alpha = f(a) \qquad (12)$$

Actually what we have determined by the calculations described above, are values of "a" and α which may and probably do differ from the true values.

This difference from the true value may be expressed thus:

$$\alpha_d = \alpha + \Delta\alpha$$

$$a_d = a + \Delta a$$

where a_d and α_d are the determined values, or we have

$$\alpha + \Delta\alpha = f(a + \Delta a) \qquad (13)$$

subtracting (12) from (13) we have

$$\Delta\alpha = f(a + \Delta a) - f(a)$$

by expanding $f(a + \Delta a)$ in a Taylor series we have

$$\Delta\alpha = f(a) + f'(a)\Delta a + \frac{f''(a)\Delta a^2}{2!} + \cdots\cdots - f(a)$$

or if we neglect as insignificant all terms containing Δa^2 or higher power, we have

$$\Delta\alpha = f'(a)\Delta a$$

Now if we sum the squares of all the terms and divide by n - 1, we obtain

$$\frac{\Sigma \Delta\alpha^2}{n-1} = \frac{\Sigma(f'(a))^2\Delta a^2}{n-1}$$

this is equivalent to

$$V(\alpha) = f'(a)^2 V(a) \qquad (14)$$

From equation (14) we can now determine the variance of α by inserting the known variance of "a" previously calculated (equation 10) and the first derivative, f'(a), therefore,

$$V(\alpha) = \left[\frac{(0.7052 + a) - (0.7052 - a)(-1)}{(0.7052 - a)^2}\right]^2 V(a)$$

$$V(\alpha) = \left[\frac{2(0.7052)}{(0.7052)^2 - 2(0.7052)a + a^2}\right]^2 V(a)$$

our previously determined values are

$$a = 0.000439$$

$$V(a) = 0.052755 \times 10^{-8}$$

so

$$V(\alpha) = \frac{(1.4104)^2 \times 0.052755 \times 10^{-8}}{(0.4973 - 1.4104(0.000439) + (0.000439)^2)^2}$$

thus

$$V(\alpha) = S^2\alpha = 0.4254 \times 10^{-8}$$

$$S(\alpha) = 0.65223 \times 10^{-4}$$

$$S(\alpha) = 0.0000652$$

Using this value of $S(\alpha)$ and the values of "t" given in the tables for our desired probability levels, we can place confidence intervals on α. Thus by our previous interpolation for 103 data points

$$P = 0.05 \; ; \quad t = 1.99$$

$$P = 0.001 \; ; \quad t = 3.375$$

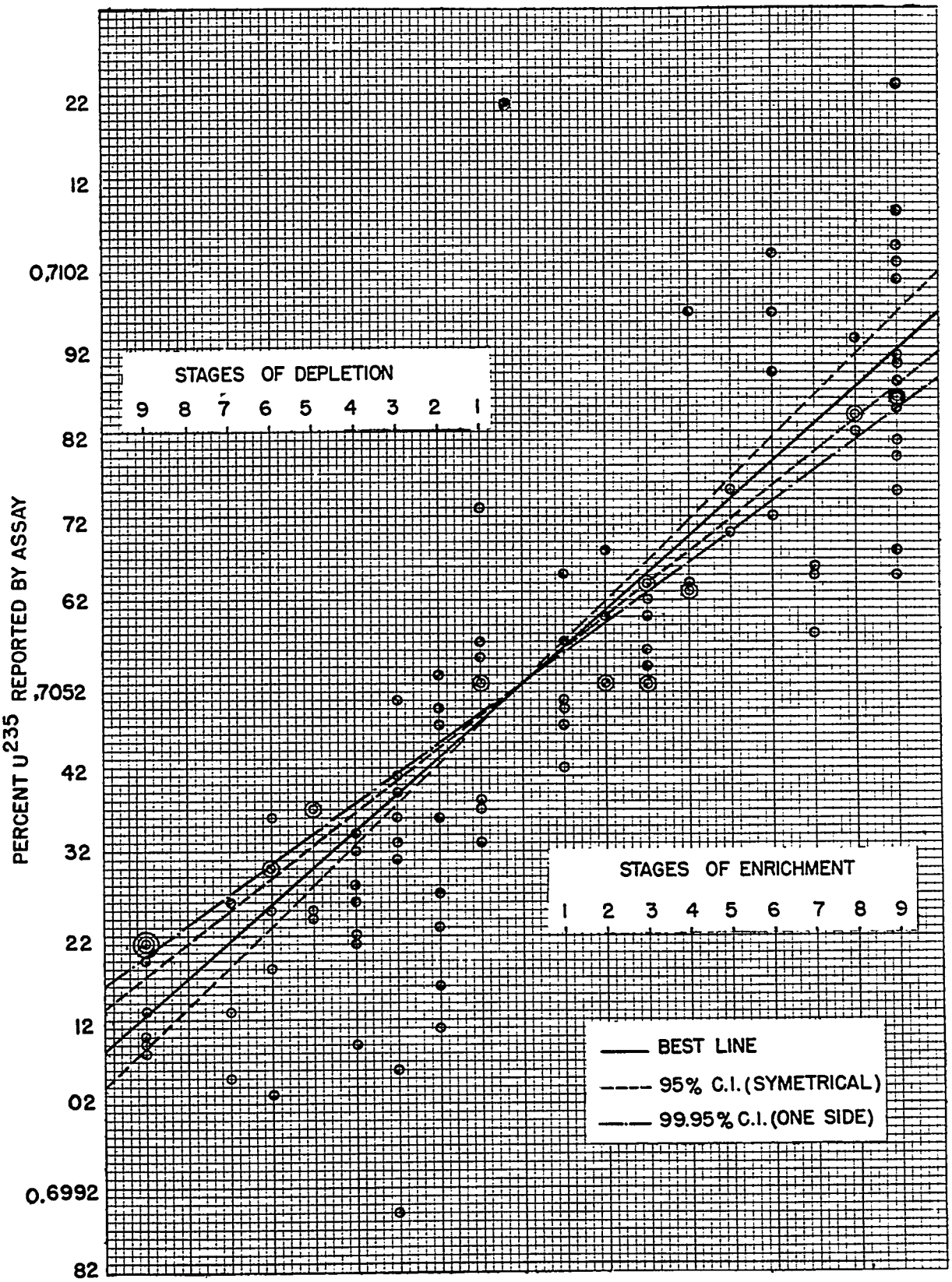
The 95% C.I. on α is

$$1.001246 \pm 1.99(0.0000652)$$

$$(1.001376 \; ; \; 1.001116)$$

and the 99.95% one sided C.I. placing a minimum value on α is

$$\alpha > 1.001026 .$$



APPENDIX E FIGURE I ASSAY RESULTS OF NINE STAGE LABORATORY BATCH OPERATION

APPENDIX F

Tabulation of Organic Complexing Agents Tested.

COMPOUND	Mol. Wt.	URANOUS					URANYL			
		Wt. Reagt. Used	Wt. U Used	REACTION	Extraction		Wt. Reagt. Used	Wt. U Used	REACTION	Extraction
					$CHCl_3$	Bu Ac				$CHCl_3$ / Bu Ac
Acetanilide	135.2	0.27	0.1	None	No	No	0.16	0.1	None	No / No
Acetoacetanilide	177.2	0.35	0.1	None	No	No	0.19	0.1	None	No / No
Acetohydroxamic Acid	75.0	0.15	0.1	None immediately reacts slowly	No	Yes (time)	0.09	0.1	Reacts slowly Orange color	No / No
2-Aceto 1-naphthol	186.2	0.37	0.1	None	No	No	0.22	0.1	None	No / No
Acetyl Acetone	100.1	0.20	0.1	Brown-green color	Yes	Yes	0.12	0.1	Orange color	No / No
N-Acetyl o-aminobenzoic Acid	179.2	0.35	0.1	None	No	No	0.21	0.1	None	No / No
Acetyl o-aminophenol	151.2	0.30	0.1	None	No	No	0.18	0.1	None	No / Slight
N-Acetyl o-anisidine	165.2	0.33	0.1	None	No	No	0.20	0.1	None	No / No
N-Acetylethanolamine	103.1	0.21	0.1	None	No	No	0.12	0.1	None	No / No
N-Acetyl N'Methylurea	116.1	0.24	0.1							
1-Acetyl 2-Thiohydantoin	158.2	0.32	0.1	None	No	No	0.19	0.1	None	No / No
Alizarin	240.2	0.48	0.1	Purple color Dye insoluble	?	?	0.29	0.1	None	No / No
1-Aminoanthraquinone	223.2	0.44	0.1	None	No	No	0.26	0.1	None	No / No
1-Amino 8-naphthol 3,6 disulfonic Acid	319.3	0.64	0.1	Precipitate	No	No	0.38	0.1	None	No / No
1-Amino 2-naphthol 4-sulfonic Acid	248.3	0.50	0.1	Color change (ppt.)	No	No	0.30	0.1	None	No / Slight
o-Aminophenol	109.1	0.22	0.1	None	No	No	0.13	0.1	Red-brown color	No / No
o-Aminophenol p-sulfonic Acid	198.2	0.40	0.1	None	No	No	0.24	0.1	None	No / No
2-Aminoresorcinol hydrochloride	161.6	0.32	0.1	None	No	No	0.19	0.1	None	No / No
5-Aminosalicylic Acid hydrochloride	189.6	0.34	0.1	Very slight. May be none. Reagent insoluble	?	?	0.20	0.1	Probably none	No / ?
Ammonium Mucate	244.1	0.49	0.1	White precipitate	No	No	0.29	0.1	Yellow color	No / No

COMPOUND	Mol. Wt.	URANOUS					URANYL				
		Wt. Reagt. Used	Wt. U Used	REACTION	Extraction		Wt. Reagt. Used	Wt. U Used	REACTION	Extraction	
					$CHCl_3$	Bu Ac				$CHCl_3$	Bu Ac
Aniline disulfonic Acid	300.	0.60	0.1	None	No	No	0.36	0.1	None	No	No
Anthragallol	256.	0.51	0.1	Possibly Emulsion and Precipitate.	?	?	0.31	0.1	Possibly. Emul.	?	?
Anthranilic Acid	137.1	0.24	0.1	None	No	No	0.14	0.1	None	No	No
d-Arabinose	150.1	0.30	0.1	None	No	No	0.18	0.1	None	No	No
Ascorbic Acid	176.1	0.36	0.1	None	No	No	0.21	0.1	Red-brown color	No	No
d-iso Ascorbic Acid	176.1	0.36	0.1	None	No	No	0.21	0.1	Red-brown color	No	No
Aurin	290.3	0.58	0.1	None	No	No	0.35	0.1	None	No	No
Aurin Tricarboxylic Acid	425.3	0.85	0.1	None	No	No	0.51	0.1	None. BuAc ext. some color.(reag?)	No	?
Aurin Tricarboxylic Acid Ammonium Salt	476.3	0.95	0.1	None	No	No	0.57	0.1	None	No	No
Benzenesulfohydroxamic Acid	173.2	0.25	0.1	None	No	No	0.15	0.1	None	No	No
Benzene 1-sulfonic Acid (4azo5)8-hydroxyquinoline	329.3	0.66	0.1	None	No	No	0.40	0.1	None	No	No
Benzidine	184.2	0.36	0.1	None	No	No	0.22	0.1	None	No	No
Benzil	210.2	0.42	0.1	None	No	No	0.25	0.1	None	No	No
α Benzil Dioxime	240.3	0.48	0.1	None	No	No	0.29	0.1	None	No	No
α Benzil Monoxime	225.2	0.45	0.1	None	No	No	0.27	0.1	None	No	No
Benzoin	254.3	0.51	0.1	None	No	No	0.31	0.1	None	No	No
α Benzoin Oxime	227.3	0.45	0.1	None	No	No	0.27	0.1	None	No	No
o-Benzoylbenzoic Acid	244.2	0.49	0.1	None	No	No	0.29	0.1	None	No	No
Benzoylcarbinol	136.1	0.27	0.1	None. Yellow tinge in $CHCl_3$	Slight	No	0.16	0.1	None	No	No

COMPOUND	Mol. Wt.	URANOUS					URANYL				
		Wt. Reagt. Used	Wt. U Used	REACTION	Extraction		Wt. Reagt. Used	Wt. U Used	REACTION	Extraction	
					$CHCl_3$	Bu Ac				$CHCl_3$	Bu Ac
Benzoylformic Acid	150.1	0.30	0.1	Tan precipitate	Yes	Yes	0.18	0.1	None	No	No
Betaine Hydrochloride	153.6	0.31	0.1	None	No	No	0.19	0.1	None	No	No
Brilliant Yellow	652.0	1.30	0.1	Dark color	No	No	0.78	0.1	Dark color	No	No
p-Bromo o-nitrosophenol	187.9	0.38	0.1	None	No	No	0.23	0.1	None	No	No
p-tert.Butyl catechol	166.2	0.33	0.1	Slight	Slight	Slight	0.20	0.1	None	No	No
Cacotheline	462.4	0.92	0.1	Intense color	No	No	0.55	0.1	None	No	No
d-Camphoric Acid	200.2	0.40	0.1	None	No	No	0.24	0.1	None	No	No
Carminic Acid	492.4	0.98	0.1	None	No	No	0.59	0.1	None	No	No
p-Chlorophenoxyacetic Acid	186.6	0.37	0.1	White-green precipitate	Yes	Yes	0.22	0.1	None	No	No
Chromotropic Acid	356.3	0.71	0.1	Slight	No	No	0.43	0.1	Dark red color	No	No
Chrysoidin R	248.7	0.49	0.1	None	No	No	0.29	0.1	None	No	No
Cinchonine	294.4	0.59	0.1	Hydrolyzed uranous	No	No	0.35	0.1	Yellow color	No	No
Citric Acid	192.1	0.38	0.1	None	No	No	0.23	0.1	None	No	No
Congo Red	696.7	1.39	0.1	Acid form of Congo Red precipitated.	No	No	0.83	0.1	Same as Uranous	No	No
Cresotinic Acid	152.1	0.30	0.1	White-green precipitate	Yes	No	0.18	0.1	None	No	No
Cupferron	155.2	0.31	0.1	Tan precipitate	Yes	Yes	0.19	0.1	Yellow-orange precipitate	No	No
Curcumin	368.4	0.74	0.1	None	No	No	0.44	0.1	Yellow complex extracted	Yes	Yes
Dextrose	180.2	0.36	0.1	None	No	No	0.22	0.1	None	No	No
Diacetone Alcohol	116.2	0.23	0.1	None	No	No	0.14	0.1	None	No	No
Diacetyl Monoxime	101.1	0.20	0.1	None	No	No	0.12	0.1	None	No	No
1,8 Diaminonaphthalene	158.2	0.32	0.1	None	No	No	0.19	0.1	None	No	No

COMPOUND	Mol. Wt.	URANOUS					URANYL				
		Wt. Reagt. Used	Wt. U Used	REACTION	Extraction		Wt. Reagt. Used	Wt. U Used	REACTION	Extraction	
					$CHCl_3$	Bu Ac				$CHCl_3$	Bu Ac
Dibenzoylmethane	224.3	0.45	0.1	Brown compound extracted	Yes	Yes	0.27	0:1	Orange color in presence of alcohol	No	No
5,7 Dibromo 8-hydroxy-quinoline	303.0	0.60	0.1	Precipitate. Incomplete extraction	Yes	Yes	0.36	0.1	Precipitate. Incomplete extraction	Yes	Yes
Dicyandiamidine sulfate	338.3	0.68	0.1	White precipitate	No	No	0.41	0.1	None	No	No
Diethanolamine	105.1	0.21	0.1	Green precipitate	No	No	0.13	0.1	Yellow precipitate	No	No
Diethylenetriamine	103.2	0.21	0.1	Green precipitate	No	No	0.13	0.1	Yellow precipitate	No	No
1,5 Dihydroxyanthra-quinone	240.2	0.48	0.1	None	No	No	0.29	0.1	None	No	No
2,4 Dihydroxybenzaldehyde	138.1	0.28	0.1	None	No	No	0.17	0.1	Orange color with ammonium hydroxide	No	No
2,4 Dihydroxybenzoic Acid	154.1	0.31	0.1	None	No	No	0.19	0.1	None	No	No
3,4 Dihydroxydiphenyl	186.2	0.37	0.1	None	No	No	0.22	0.1	None	No	No
1,8 Dihydroxynaphthalene 3,6 disulfonic Acid	356.3	0.71	0.1	None	No	No	0.43	0.1	Water soluble red complex	No	No
α Dimethylaminoglycerol	119.2	0.24	0.1	Green precipitate	No	No	0.14	0.1	Yellow precipitate	No	No
Dimethylglyoxime	116.1	0.23	0.1	None	No	No	0.14	0.1	None	No	No
2,4 dinitrophenylhydrazine	198.1	0.40	0.1	None	No	No	0.24	0.1	Red color in BuAc may be reagent only	No	?
3,5 Dinitrosalicylic Acid	246.1	0.49	0.1	White precipitate	No	Yes	0.29	0.1	Extract may be just reagent.	No	?
2,4 Dinitrosoresorcinol	168.0	0.34	0.1	None	No	No	0.20	0.1	None	No	No
s-Diphenylcarbazide	242.3	0.48	0.1	None	No	No	0.29	0.1	None	No	No
s-Diphenylcarbazone	240.3	0.48	0.1	None	No	No	0.29	0.1	None	No	No
Diphenylthiocarbazide	258.3	0.52	0.1	None	No	No	0.31	0.1	None	No	No
s-Diphenylthiourea	228.3	0.46	0.1	None	No	No	0.28	0.1	None	No	No
Dipyricrylamine	439.2	0.88	0.1	None	No	No	0.53	0.1	None	No	No

COMPOUND	Mol. Wt.	URANOUS					URANYL				
		Wt. Reagt. Used	Wt. U Used	REACTION	Extraction		Wt. Reagt. Used	Wt. U Used	REACTION	Extraction	
					$CHCl_3$	Bu Ac				$CHCl_3$	Bu Ac
α, α′ Dipyridyl	156.2	0.31	0.1	None	No	No	0.19	0.1	None	No	No
Dithiooxamide	120.2	0.24	0.1	None	No	No	0.14	0.1	None	No	No
Ethanolamine	61.1	0.12	0.1	Green precipitate	No	No	0.07	0.1	Yellow precipitate	No	No
Ethyl Benzoylpyruvate	220.0	0.44	0.1	Red-brown extract	Yes	Yes	0.26	0.1	None	No	No
Ethyl Lactate	118.1	0.24	0.1	None	No	No	0.14	0.1	None	No	No
Ethylthioglycolic Acid	120.2	0.24	0.1	White precipitate green extract	Yes	Yes	0.14	0.1	None	No	No
Furfural	96.1	0.19	0.1	None	No	No	0.11	0.1	None	No	No
Furfuraldoxime	111.1	0.22	0.1	None	No	No	0.13	0.1	None	No	No
Furfuramide	268.3	0.54	0.1	None	No	No	0.32	0.1	None	No	No
Furfuryl Alcohol	98.1	0.20	0.1	None	No	No	0.12	0.1	None	No	No
α Furil Dioxime	238.2	0.48	0.1	None	No	No	0.29	0.1	None	No	No
Gallic Acid	188.1	0.38	0.1	None	No	No	0.23	0.1	None	No	No
Gallocyanine	300.3	0.60	0.1	None	No	No	0.36	0.1	None	No	No
Gluconic Acid	196.2	0.39	0.1	None	No	No	0.23	0.1	None	No	No
Glutamic Acid	147.1	0.29	0.1	None	No	No	0.17	0.1	None	No	No
Glycerol	92.1	0.18	0.1	None	No	No	0.11	0.1	None	No	No
Glycine	75.1	0.15	0.1	None	No	No	0.09	0.1	None	No	No
Glycolic Acid	76.1	0.15	0.1	None	No	No	0.09	0.1	None	No	No
Hematoxylin	356.3	0.71	0.1	Purple color	No	No	0.43	0.1	Orange-red	No	Yes (?)
Hippuric Acid	179.2	0.36	0.1	Green solution in BuAc.	No	Yes	0.22	0.1	None	No	No
Hydroxyethyl-ethylenediamine	104.2	0.21	0.1	Green precipitate	No	No	0.13	0.1	Yellow precipitate	No	No

COMPOUND	Mol. Wt.	URANOUS					URANYL				
		Wt. Reagt. Used	Wt. U Used	REACTION	Extraction		Wt. Reagt. Used	Wt. U Used	REACTION	Extraction	
					$CHCl_3$	Bu Ac				$CHCl_3$	Bu Ac
3 Hydroxy 2 naphthoic Acid	188.2	0.38	0.1	Green solution in BuAc.	No	Yes	0.23	0.1	Yellow BuAc extract (may be reagent)	No	Yes
p-Hydroxyphenylglycine	167.2	0.33	0.1	None	No	No	0.20	0.1	None	No	No
8-Hydroxyquinoline	145.2	0.29	0.1	Not complete (may oxidize uranous)	Yes	Yes	0.17	0.1	Red-orange color	Yes	Yes
8-Hydroxyquinoline 5-sulfonic Acid	261.3	0.52	0.1	None	No	No	0.31	0.1	None	No	No
7-Iodo 8-hydroxyquinoline 5-sulfonic Acid	351.1	0.70	0.1	Slight color	No	No	0.42	0.1	Orange color	No	No
Isatin	147.1	0.29	0.1	None	No	No	0.17	0.1	None	No	No
Isatin β oxime	162.1	0.32	0.1	None	No	No	0.19	0.1	None	No	No
Isonitrosoacetylacetone	129.1	0.26	0.1	None	No	No	0.16	0.1	None	No	No
Lactose	360.3	0.72	0.1	None	No	No	0.43	0.1	None	No	No
Levulose	180.2	0.36	0.1	None	No	No	0.22	0.1	None	No	No
Malonamide	102.1	0.20	0.1	None	No	No	0.12	0.1	None	No	No
Mannitol	182.2	0.36	0.1	None	No	No	0.22	0.1	None	No	No
Melamine	126.1	0.25	0.1	None	No	No	0.15	0.1	None	No	No
2-Methyl 2-nitro 1,3 propanediol	135.0	0.26	0.1	None	No	No	0.16	0.1	None	No	No
2-Methyl 2,4 pentandiol	118.2	0.24	0.1	None	No	No	0.14	0.1	None	No	No
Methyl Red	269.3	0.54	0.1	None	No	No	0.32	0.1	None	No	No
Methyl Salicylate	152.1	0.30	0.1	None	No	No	0.18	0.1	None	No	No
Morin	338.3	0.68	0.1	Color change emulsion with $CHCl_3$	No	No	0.41	0.1	Color change emulsion with $CHCl_3$	No	No
Mucic Acid	210.1	0.42	0.1	None	No	No	0.25	0.1	None	No	No
Naphthalene 1-sulfonic acid (4azo5)8-hydroxy-quinoline	379.0	0.76	0.1	Precipitate	No	Slight	0.46	0.1	Precipitate	No	No

COMPOUND	Mol. Wt.	URANOUS					URANYL				
		Wt. Reagt. Used	Wt. U Used	REACTION	Extraction		Wt. Reagt. Used	Wt. U Used	REACTION	Extraction	
					$CHCl_3$	Bu Ac				$CHCl_3$	Bu Ac
2-Naphthol 3,6 disulfonic Acid	304.3	0.61	0.1	Precipitate	No	No	0.37	0.1	Red color	No	No
1-Naphthlamine 8-sulfonic Acid	223.2	0.45	0.1	None	No	No	0.27	0.1	None	No	No.
Neocupferron	205.2	0.41	0.1	Dark precipitate precipitate with BuAc	Yes	?	0.25	0.1	Difficult to tell because of the intense color of the reagent.	?	?
p-Nitroaniline o-sulfonic Acid	218.2	0.44	0.1	Yellow color	No	No	0.26	0.1	Reagent masks any uranyl effect.	?	?
p-Nitrobenzeneazo-resorcinol	273.2	0.55	0.1	Precipitate	No	No	0.33	0.1	Precipitate	No	No
m-Nitrobenzeneazo-resorcinol	259.2	0.52	0.1	Precipitate	No	No	0.31	0.1	None	No	No
Nitroguanidine	104.1	0.21	0.1	None	No	No	0.13	0.1	None	No	No
3-Nitrosalicylic Acid	201.1	0.40	0.1	Slight extraction in BuAc.	No	Yes	0.24	0.1	Indefinite. May be reagent.	No	Yes(?)
iso-Nitrosoacetophenone	149.1	0.30	0.1	None	No	No	0.18	0.1	None	No	No
αNitrosoβNaphthol	173.2	0.35	0.1	None	No	No	0.21	0.1	None	No	No
βNitrosoαNaphthol	173.2	0.35	0.1	Some reaction. Masked by reagent.	Yes	Yes	0.21	0.1	Similar to uranous. Less easy to distinguish.	?	?
Nitrosoresorcinol-Na Salt	183.1	0.37	0.1	Brown precipitate	No	No	0.22	0.1	Brown precipitate	No	No
Oxalic Acid	90.0	0.18	0.1	White-green precipitate	No	No	0.11	0.1	None	No	No
Oxamide	88.1	0.17	0.1	None	No	No	0.10	0.1	None	No	No
Pentaerythritol	136.2	0.27	0.1	None	No	No	0.16	0.1	None	No	No
N-Phenylanthranilic Acid	213.2	0.43	0.1	Color change. May oxidize uranous.	Yes	?	0.26	0.1	Slight, if any.	?	?
o-Phenylenediamine	108.1	0.22	0.1	None	No	No	0.13	0.1	It reacts but masked by reagent.	?	Yes
N-Phenylglycine	151.2	0.30	0.1	Slight reaction	Yes	Slight	0.18	0.1	None	No	No
Phenylglyoxylic acid oxime	165.1	0.33	0.1	White-green precipitate	No	Yes	0.20	0.1	Yellow color with ethanol.	No	Yes
Phenylthiohydantoic Acid	210.3	0.42	0.1	None	No	No	0.25	0.1	None	No	No

SECRET

SECRET

COMPOUND	Mol. Wt.	URANOUS					URANYL				
		Wt. Reagt. Used	Wt. U Used	REACTION	Extraction		Wt. Reagt. Used	Wt. U Used	REACTION	Extraction	
					$CHCl_3$	Bu Ac				$CHCl_3$	Bu Ac
Phenylthiourea	136.2	0.27	0.1	None	No	No	0.16	0.1	None	No	No
o-Phthalic Acid	166.1	0.33	0.1	None	No	No	0.20	0.1	None	No	No
Picric Acid	229.1	0.46	0.1	Precipitate	No	No	0.28	0.1	Slight in BuAc.	No	Slight
Pinacol	118.2	0.24	0.1	Yes	No	No	0.14	0.1	Yes	No	No
Potassium Ethyl Xanthate	160.3	0.32	0.1	Precipitate	No	Yes	0.20	0.1	Red precipitate	No	Yes
iso-Propanolamine	75.1	0.15	0.1	Precipitate	No	No	0.09	0.1	Precipitate	No	No
Propylene Glycol	76.1	0.15	0.1	None	No	No	0.09	0.1	None	No	No
Purpurin	256.2	0.51	0.1	Deep color and precipitate	No	No(?)	0.31	0.1	Deep color and precipitate	No(?)	No(?)
Pyrogallol	126.1	0.25	0.1	Yes	No	No	0.15	0.1	Yes	No	No
Pyruvic Acid	88.1	0.18	0.1	Solution colored. slight extraction.	Yes	Yes	0.11	0.1	Slight	Yes	Yes
Quercetin	338.3	0.68	0.1	Yes	No	No	0.41	0.1	None	No	No
Quinalizarin	272.2	0.55	0.1	Yes	No	No	0.33	0.1	Yes	No	No
Quinolinic Acid	167.1	0.33	0.1	None	No	No	0.20	0.1	None	No	No
Resacetophenone	152.1	0.30	0.1	None	No	No	0.18	0.1	None	No	No
β Resorcylic Acid	154.1	0.31	0.1	Yes	No	Slight	0.19	0.1	None	No	No
Rufigallol	304.2	0.61	0.1	None	No	No	0.37	0.1	None	No	No
Salicylaldehyde	122.1	0.24	0.1	None	No	No	0.14	0.1	None	No	No
Salicylaldoxime	137.7	0.27	0.1	Yes	Some	Slight	0.16	0.1	Yes	Some	Slight
Salicylic Acid	138.0	0.27	0.1	White-green precipitate with ethanol.	No	Slight	0.16	0.1	None	No	No
Sodium Alizarin sulfonate	360.3	0.72	0.1	Masked by reagent	?	?	0.43	0.1	Masked by reagent	?	?

COMPOUND	Mol. Wt.	URANOUS					URANYL				
		Wt. Reagt. Used	Wt. U Used	REACTION	Extraction		Wt. Reagt. Used	Wt. U Used	REACTION	Extraction	
					$CHCl_3$	Bu Ac				$CHCl_3$	Bu Ac
Semicarbazide hydrochloride	111.5	0.22	0.1	None	No	No	0.13	0.1	None	No	No
Sodium Diethyl Dithiocarbamate	171.0	0.34	0.1	Precipitate	Yes	Yes	0.20	0.1	Precipite (red)	Yes	Some
Sodium 2,4 Dihydroxyazobenzene 4 sulfonate	361.0	0.72	0.1	Precipitate and emulsion. Masked by reagent.	?	?	0.43	0.1	None	No	No
Sodium p-Dimethylaminoazobenzene p'-carboxylate	291.3	0.58	0.1	Slight, if any.	?	?	0.35	0.1	Masked by reagent Slight, if any.	?	?
Sodium Formaldehyde sulfoxylate	154.1	0.31	0.1	Slight white precipitate	No	No	0.19	0.1	Orange color. Reduced to uranous.	No	No
Sodium Indigodisulfonate	365.3	0.73	0.1	None	No	No	0.44	0.1	None	No	No
Sodium p-Nitrobenzeneazosalicylate	309.2	0.61	0.1	Precipitate	No	Slight	0.37	0.1	Precipitate	No	No
Sodium Rhodizonate	214.0	0.43	0.1	Green Color	No	No	0.26	0	Red color	No	No
Succinic Acid	118.1	0.24	0.1	White precipitate	No	No	0.14	0.1	None	No	No
Sulfosalicylic Acid	218.2	0.44	0.1	None	No	No	0.26	0.1	None	No	No
Tannic Acid	322.2	0.64	0.1	Precipitate	No	No	0.38	0.1	Orange color	No	No
Tartaric Acid	150.0	0.30	0.1	White precipitate	No	No	0.18	0.1	None	No	No
Tetramethylthiouram Disulfide	240.0	0.48	0.1	None	No	No	0.29	0.1	None	No	No
Thioglycolic Acid	92.1	0.18	0.1	Precipitate	No	No	0.11	0.1	None	No	No
Thiosalicylic Acid	154.0	0.31	0.1	Precipitate	Yes	Yes	0.19	0.1	None	No	No
Titan Yellow	662.7	1.32	0.1	Precipitate	No	No	0.79	0.1	Precipitate	No	No
Triethanolamine	149.0	0.30	0.1	Precipitate	No	No	0.18	0.1	Precipitate	No	No
Triethylenetetramine	146.0	0.29	0.1	Precipitate	No	No	0.17	0.1	Precipitate	No	No
Trifluoroacetylacetone	154.0	0.31	0.1	Precipitate	Yes	Yes	0.18	0.1	Orange color	Slight	Slight
Uric Acid	168.0	0.34	0.1	None	No	No	0.20	0.1	None	No	No
Violuric Acid	157.0	0.31	0.1	Probably hydrolysis of uranous	No	No	0.19	0.1	None	No	No

APPENDIX G

Derivation of the Exchange Rate Constant, k_1

The exchange reaction may be represented by the equation:

$$\dot{U}O_2^{+2} + U^{+4} \underset{k_1}{\overset{k_1}{\rightleftharpoons}} \dot{U}^{+4} + UO_2^{+2}$$

The oxidation reaction by the equation:

$$\dot{U}^{+4} \xrightarrow{k_2} \dot{U}O_2^{+2}$$

$$U^{+4} \xrightarrow{k_2} UO_2^{+2}$$

Let $(\dot{U}O_2^{+2}) = A$; $(U^{+4}) = B$; at $t = 0$

$(\dot{U}^{+4}) = x$; $(UO_2^{+2}) = y$; at $t = t$

$$R \equiv \frac{(\dot{U}^{+4})}{(U^{+4})}$$

$$\frac{dR}{dt} = \frac{(U^{+4})\frac{d(\dot{U}^{+4})}{dt} - (\dot{U}^{+4})\frac{d(U^{+4})}{dt}}{(U^{+4})^2}$$

$$\frac{d(\dot{U}^{+4})}{dt} = k_1(\dot{U}O_2^{+2})(U^{+4}) - k_1(\dot{U}^{+4})(UO_2^{+2}) - k_2(\dot{U}^{+4})$$

$$\frac{d(U^{+4})}{dt} = k_1(\dot{U}^{+4})(UO_2^{+2}) - k_1(\dot{U}O_2^{+2})(U^{+4}) - k_2(U^{+4})$$

$$\frac{dR}{dt} = \frac{(U^{+4})[k_1(\dot{U}O_2^{+2})(U^{+4}) - k_1(\dot{U}^{+4})(UO_2^{+2}) - k_2(\dot{U}^{+4})] - (\dot{U}^{+4})[k_1(\dot{U}^{+4})(UO_2^{+2}) - k_1(UO_2^{+2})(U^{+4}) - k_2(U^{+4})]}{[(U^{+4})]^2}$$

$$\frac{dR}{dt} = k_1(\dot{U}O_2^{+2}) - k_1\frac{(\dot{U}^{+4})(UO_2^{+2})}{(U^{+4})} - \frac{k_2(\dot{U}^{+4})}{(U^{+4})} - \frac{k_1(\dot{U}^{+4})^2(UO_2^{+2})}{[(U^{+4})]^2} + \frac{k_1(\dot{U}O_2^{+2})(\dot{U}^{+4})}{(U^{+4})} + \frac{k_2(\dot{U}^{+4})}{(U^{+4})}$$

$$\frac{1}{k_1}\frac{dR}{dt} = (\dot{U}O_2^{+2}) - R(UO_2^{+2}) - R^2(UO_2^{+2}) + R(\dot{U}O_2^{+2})$$

at time t, $(\dot{U}O_2^{+2}) = A - x$; and (UO_2^{+2}) $\quad y = \frac{BR - x}{R}$

$$\frac{1}{k_1}\frac{dR}{dt} = (A - x) - (BR - x) - R(BR - x) + R(A - x)$$

$$\frac{1}{k_1}\frac{dR}{dt} = A + (A - B)R - BR^2$$

$$k_1 \int dt = \int \frac{dR}{A + (A - B)R - BR^2}$$

$$k_1 t = \frac{1}{A + B} \ln \frac{-B - BR}{A - BR} + C$$

Evaluating C at t = 0, and R = 0

$$C = \frac{1}{A + B} \ln \frac{-B}{A}$$

$$k_1 t = \frac{1}{A + B} \ln \frac{A(B + BR)}{B(A - BR)}$$

$$k_1 t = \frac{1}{A + B} \ln \frac{A(1 + R)}{(A - BR)}$$

APPENDIX H

Evaluation of R

The value of R at a time t is obtained by solving simultaneous equations derived from experimental results.

The reaction may be represented by the equation:

$$\overset{*}{U}O_2^{+2} + U^{+4} \rightleftharpoons \overset{*}{U}^{+4} + UO_2^{+2}$$

and at time t we let

x = Micrograms (γ) uranium present as $\overset{*}{U}^{+4}$

z = Micrograms (γ) uranium present as U^{+4}

$$\text{then } R = \frac{x}{z} \qquad (1)$$

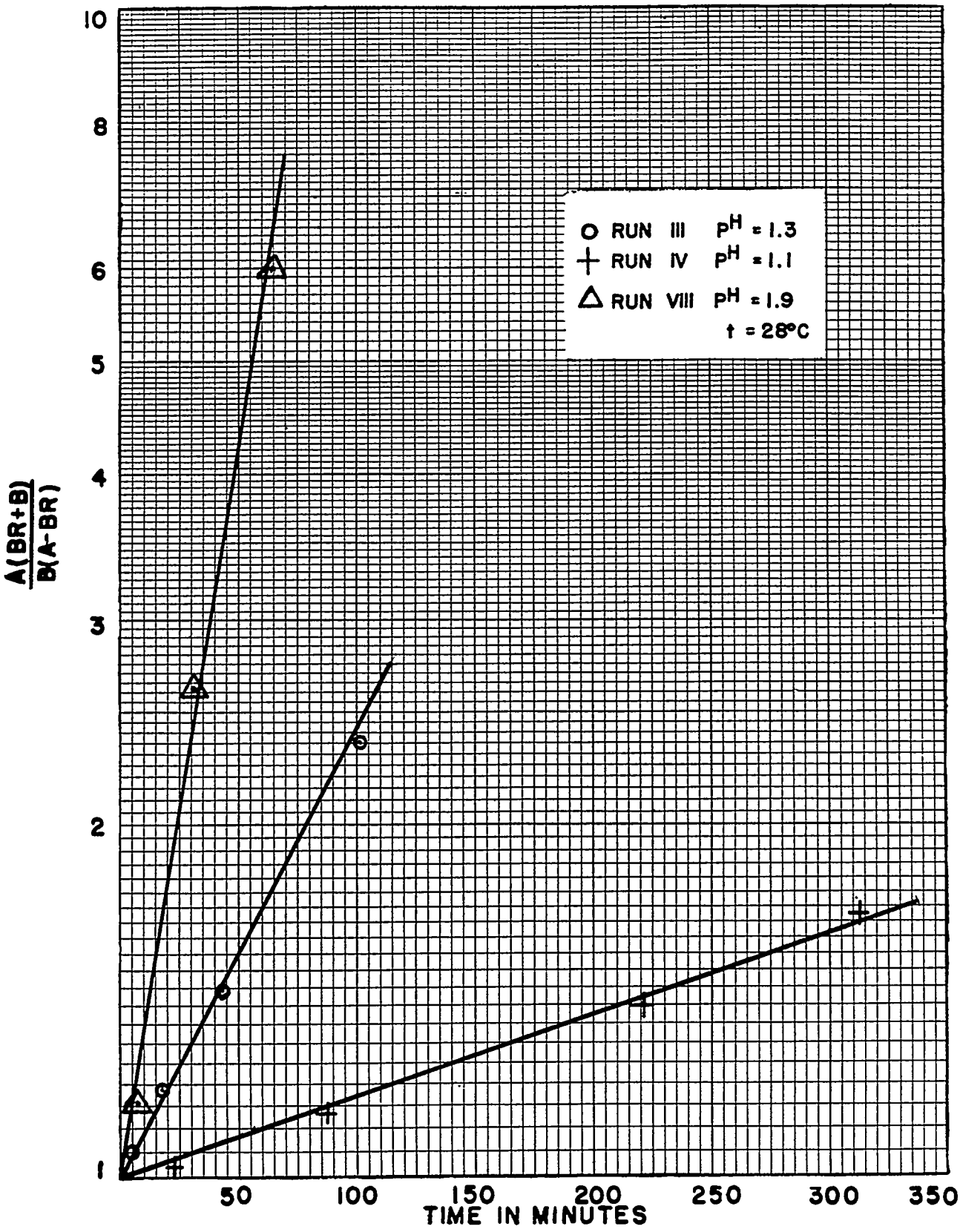
Two milliliter aliquots removed from the system at various times (t) were subjected to an extraction to remove the tetravalent uranium. The total uranium thus extracted is determined colorimetrically and gives the first equation:

$$x + z = \text{tetravalent uranium extracted from 2 ml of system} \qquad (2)$$

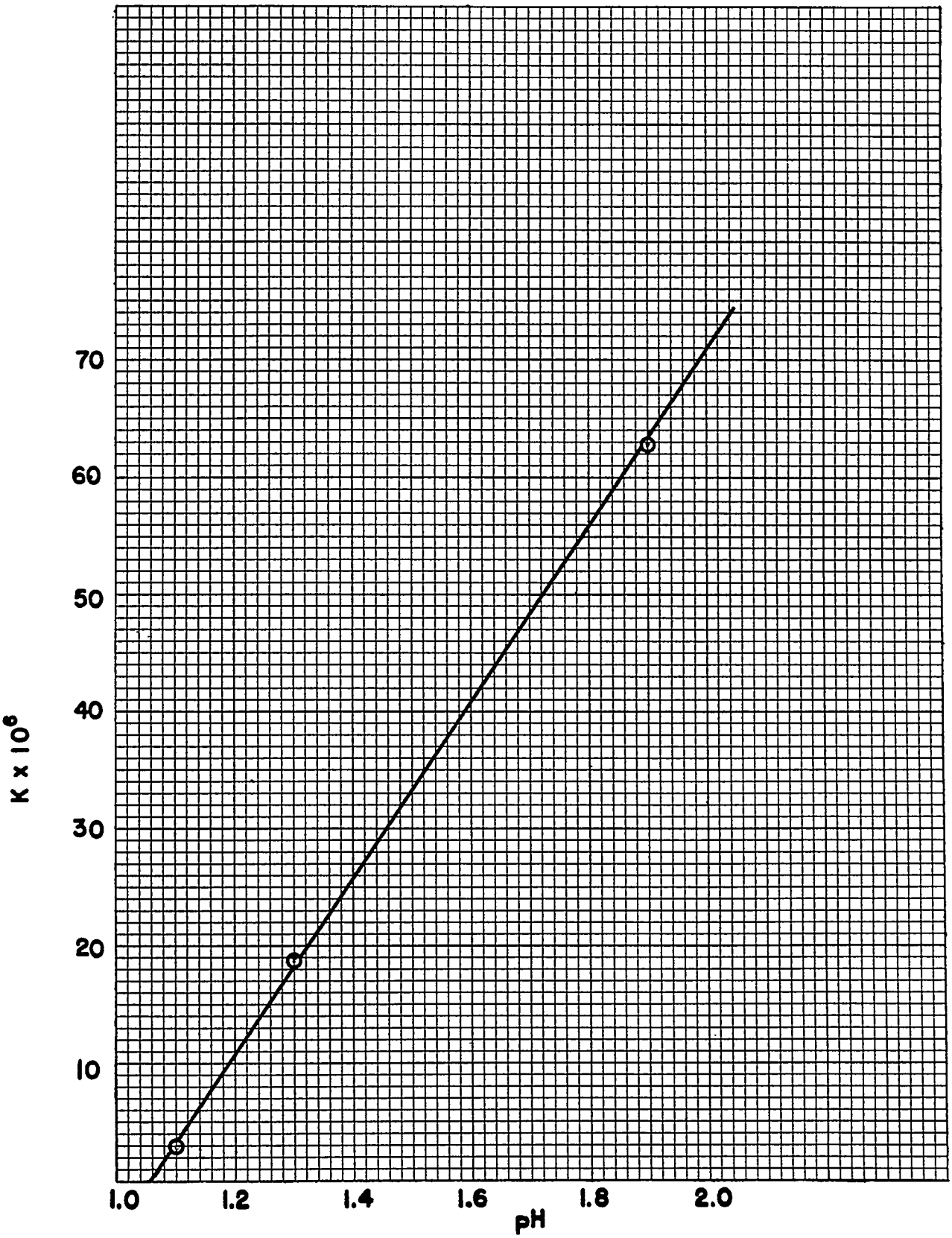
An alpha count of the uranium is also made in order to determine its activity as c/m/γ. Since the activity of $\overset{*}{U}$ is known, 21.2 c/m/γ, and also that of the U, 0.4 c/m/γ, a second equation may be set up.

$$21.2x + .4z = \text{total number of counts per minute of tetravalent uranium extracted from 2 ml aliquot.} \qquad (3)$$

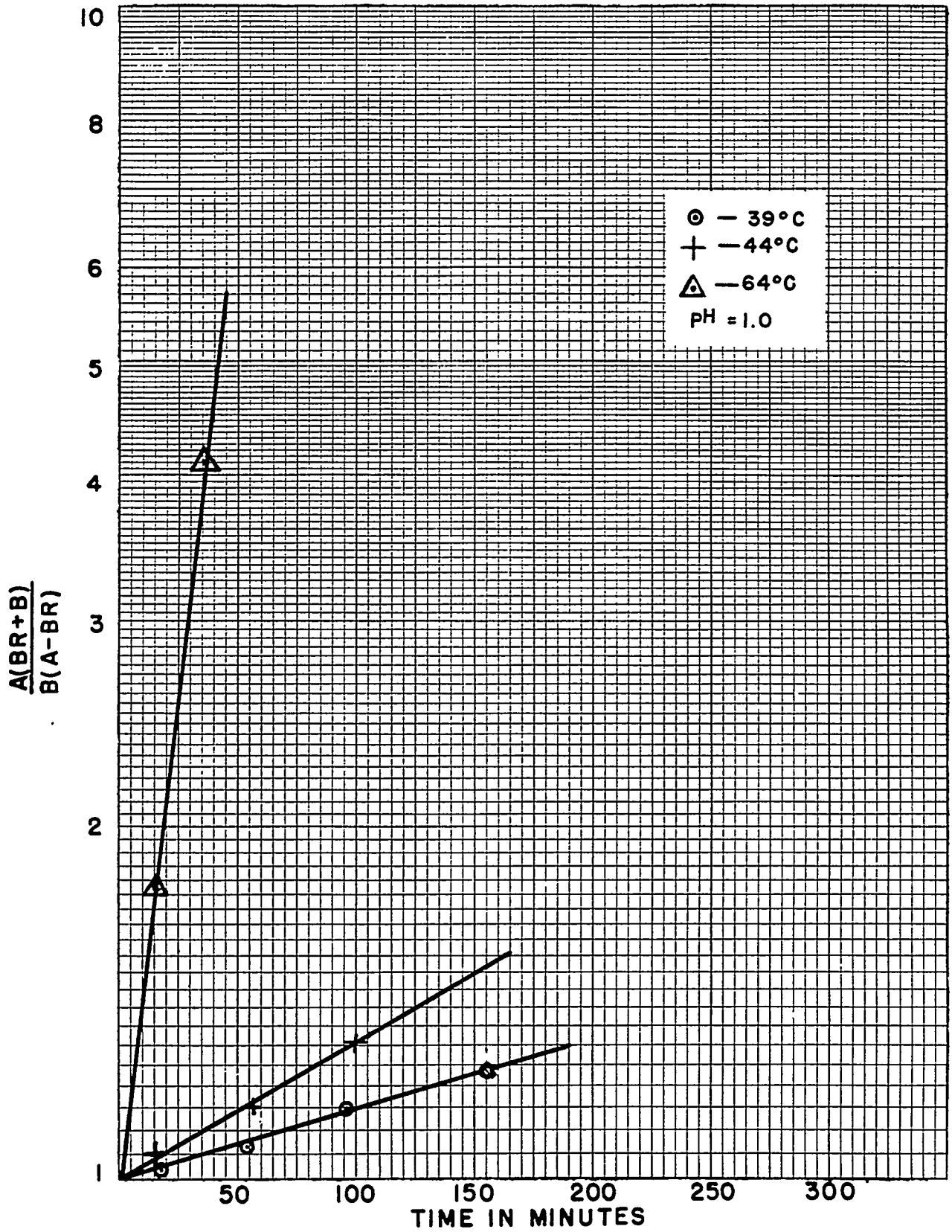
The values obtained for x and z by solving equations (2) and (3) are substituted in (1) to obtain the value of R at a known time t.



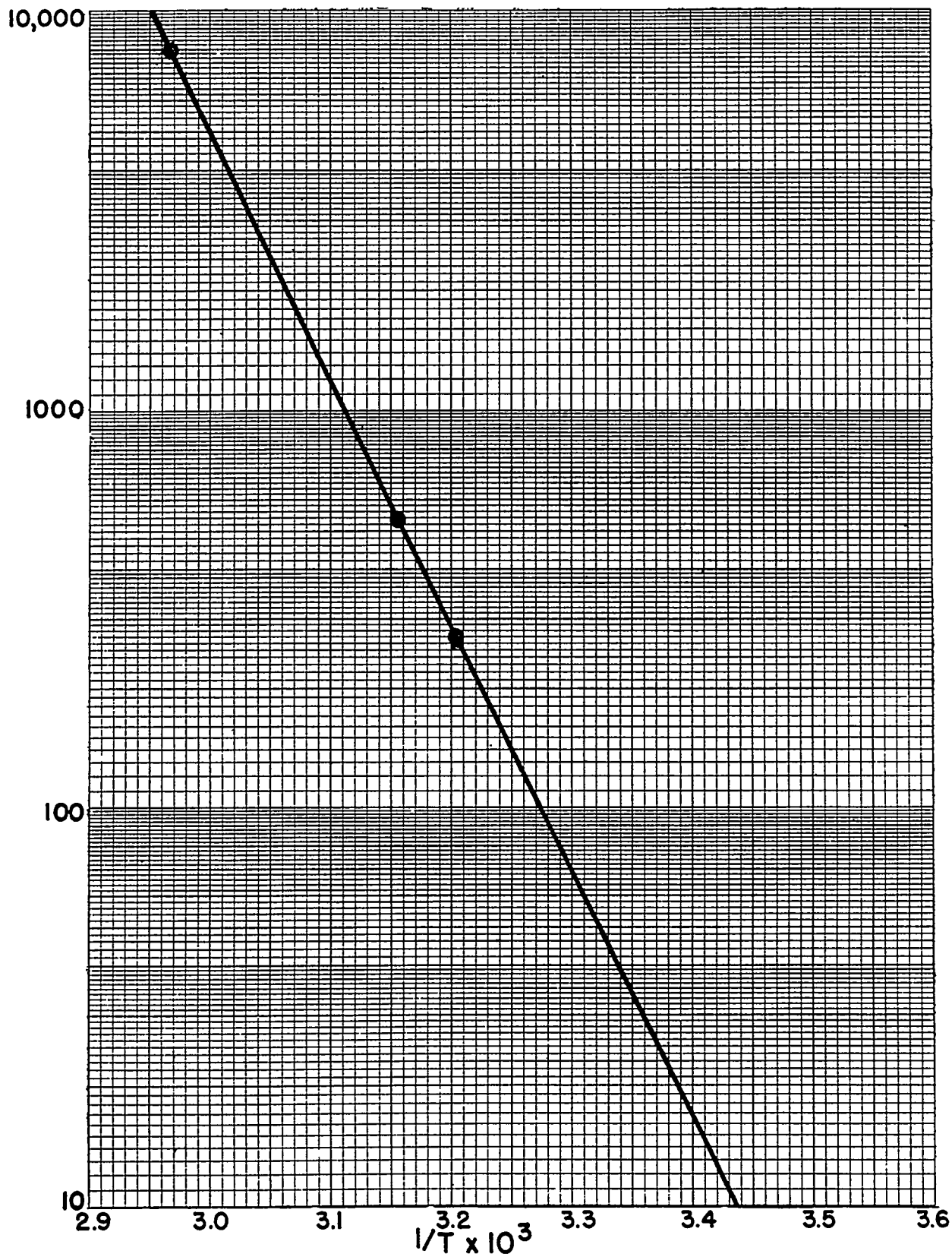
APPENDIX J FIGURE I
EFFECT OF H CONCENTRATION ON RATE OF EXCHANGE



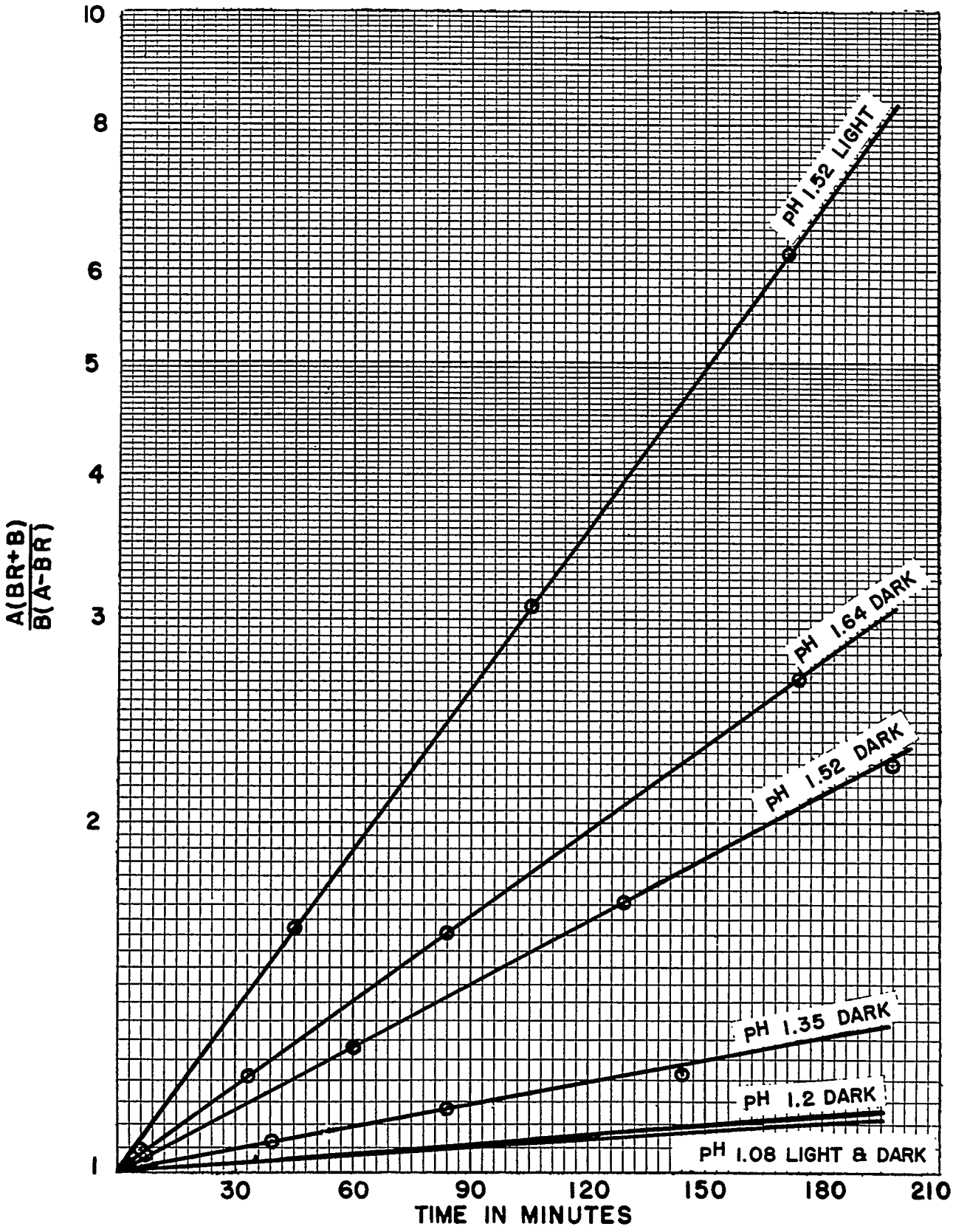
APPENDIX J FIGURE 2
REACTION RATE CONSTANT vs pH t = 28° C



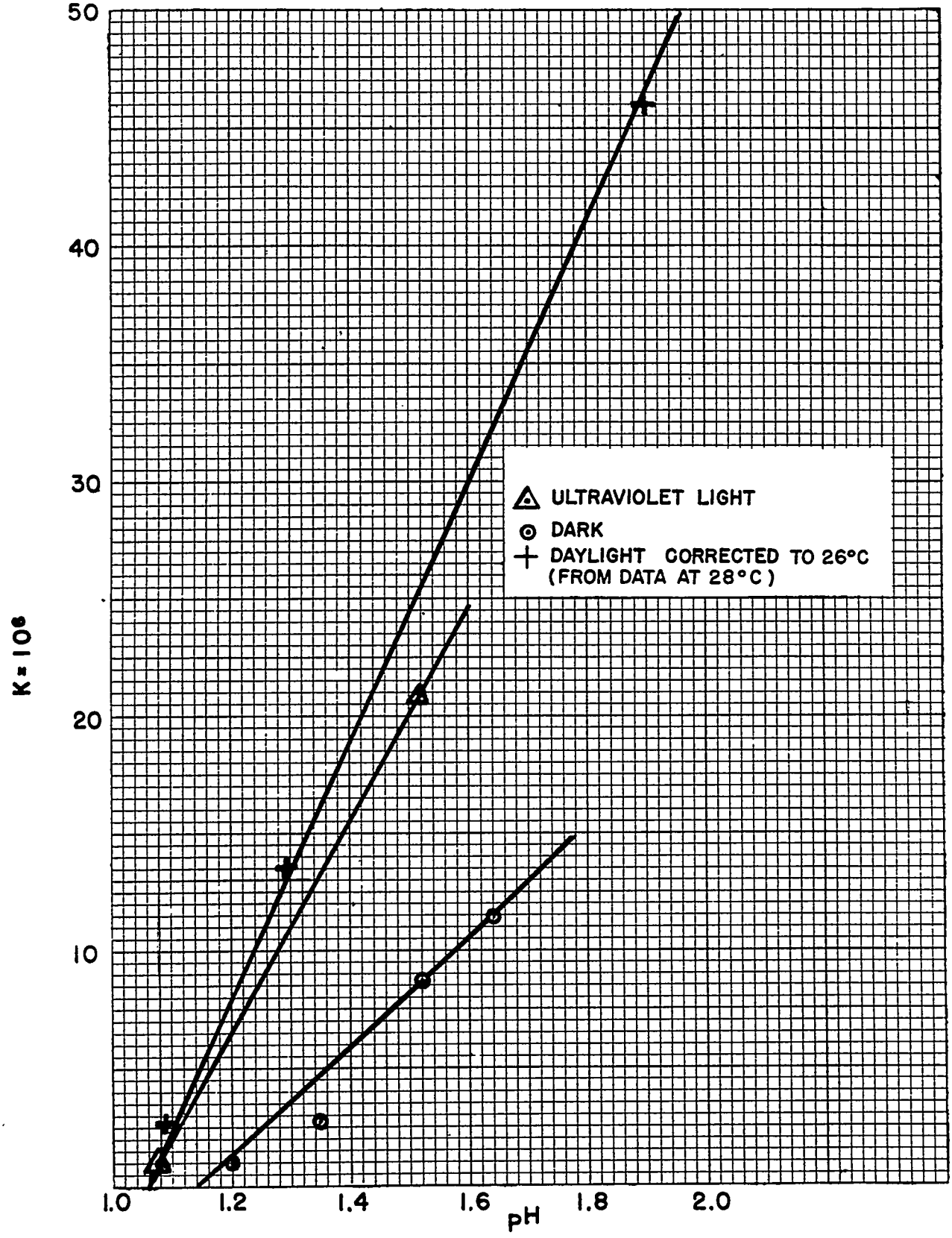
APPENDIX J FIGURE 3
EFFECT OF TEMPERATURE ON RATE OF EXCHANGE



APPENDIX J FIGURE 4 RATE CONSTANT
vs RECIPROCAL OF ABSOLUTE TEMPERATURE



APPENDIX J FIGURE 5 EFFECT OF LIGHT ON RATE OF EXCHANGE AT VARIOUS H^+ CONCS.



APPENDIX J FIGURE 6

REACTION RATE CONSTANT vs ^{pH} t = 26°C

APPENDIX K

Determination of the Ultraviolet Intensity from a Mercury Arc Source

Experiments described under "Effect of Light" in the main body of this report utilized a mercury arc lamp as a source of ultraviolet light. To determine the output of this source, a uranyl oxalate actinometer (32, 33) was employed.

The actinometer functions on the principle that ultraviolet radiation decomposes the oxalate. A permanganate titration of the total oxalate present before and after exposure measures the decomposition which has taken place. This value is related to the intensity of the ultraviolet source by the quantum yield (ϕ) which has been accurately determined by Forbes (33) as

$$\phi = \frac{.6 \text{ molecule}}{\text{quantum}}$$

Using the information given above, it is possible to set up this equation:

$$\text{Output of source} = \frac{WX(Me\text{-}me) \times 6.06 \times 10^{23}}{\phi \times t \times \frac{\text{equivalents}}{\text{mole}} \times 10^{3}}$$

where W = total weight (solution) of sample exposed

ME = number of milliequivalents/gram solution before exposure

me = number of milliequivalents/gram solution after exposure

ϕ = quantum yield

t = time of exposure (seconds)

The table below gives the results of the actinometer runs.

Run No.	Time Exposed	Wt. Sol'n Exposed (g)	.0976 N KMn^0_4 used (ml)	Millieq. per gram	Output of Source Quantum/sec x 10^{15}
1	10,089	7.3310	5.63	.075	13
2	8,100	8.2080	7.47	.089	11
3	10,920	9.4324	6.78	.070	18
					Average = 14

It should be pointed out that the uranyl oxalate solution comprising the actinometer was exposed in the same corex cell and in the identical location with respect to the ultraviolet source as used subsequently in the "exchange" runs.

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